COLLEGE AND UNIVERSITY SERIES

QUANTUM MECHANICS

by John R. Merrill

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This material is designed to be used with any Hewlett-Packard system with the BASIC program language such as the 9830A, Educational BASIC, and the 2000 and 3000 series systems.

PREFACE

This unit shows you ways in which the computer can extend your knowledge and understanding of introductory quantum mechanics. The unit presents numerical solutions to Schrödinger's equation; the solutions are easy to understand and yet include solutions to many Schrödinger equation problems which can't be handled by analytic methods. The emphasis in the unit will be on ways the computer can extend the quantum mechanics you understand. The unit assumes some knowledge of introductory quantum mechanics, specifically analytic solutions for the infinite square well, and matching wave functions at boundaries.

Your instructor can assign chapters and exercises out of this unit in much the same way as out of a textbook. Lectures on the material may be presented, but you should be able to understand the material without lectures. The harder exercises can be used as the basis of projects if your instructor wishes.

Each chapter in the unit starts with a brief discussion of the physics discussion of the physics discussed in the chapter and then moves on to an explanation of the numerical procedure used with the computer. Exercises follow with one exercise completely worked out in the text so that you can see what a sample solution looks like. This sample exercise is sometimes a problem for which the answer is already known and therefore provides an extra check on the computer method. Some exercises are marked with asterisks. One asterisk means the exercise is fairly demanding while two asterisks indicates a very challenging problem. Numerical methods will not be discussed much in the text; there is a section in the appendix which discusses the half-step integration used in the first two chapters.

There are, of course, other problems concerning quantum mechanics which can be done with a computer. On the one hand, the computer can calculate energies and wave functions for analytic solutions like the finite square well or the harmonic oscillator or the hydrogen atom. On the other hand; the computer can sometimes do the matrix operations which occur in perturbation theory or in the matrix formulation of quantum mechanics. These other applications are not included because this unit emphasizes extensions of introductory quantum mechanics byond ordinary analytic methods.

There are also ways to solve the Schrödinger equation directly as a partial differential equation using the computer. These applications will not be included because of their extra sophistication. When dealing with partial differential equations on a computer, you have to worry about convergence, stability, and representation. Even though the one dimensional, time-dependent Schrödinger equation is a relatively simple partial differential equation of the parabolic type, the most straightforward approaches using a computer turn out to be unstable. The solutions for such problems are discussed in reference (1).

The three-dimensional, time-independent Schrödinger equation is an example of an elliptic partial differential equation (as are Laplace's equation and Poisson's equation). These solutions are more straightforward; examples of elliptic partial differential equations are discussed in references (2) and (3). Most of the interesting potentials of quantum mechanics have symetries which do not allow you to use partial differential equation techniques.

Throughout the booklet the atomic units introduced by Hartree (Proc. Camb. Phil. Soc. 24, 89 (1928)) will be used. The units have the advantage that the numbers being calculated stay near 1; numbers rarely get too small or too large for the computer. Atomic units are often used in quantum mechanics; the units have the effect of setting $h = e = m_e = 1$. In atomic units.

quantity	unit
charge	e
mass	m_e
distance	first Bohr radius (.52917Å)
velocity	first Bohr speed (2.2×10^8 cm/sec)
energy	twice the ionization potential of hydrogen (27.21eV)
time	first Bohr period/2π(2.419×10^{-17} sec)

Often graphical output is useful. If you have a plotter or a CRT terminal available, fine. If not, terminal plotting (using the teletype to plot a graph) can be helpful. The appendix gives a program to convert printing programs (programs which type out lists of numbers) to programs which plot on the terminal. This terminal plotting will be used several times in the unit to give you several examples.

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CHAPTER ONE: ONE-DIMENSIONAL BOUND STATES

INTRODUCTION

The one-dimensional, time-independent, Schrödinger equation for the wave function, P, of a particle in a potential, V(x), is

$$-\frac{\hbar^2}{2m} \frac{d^2P(x)}{dx^2} + V(x)P(x) = EP(x) \qquad (1)$$

where E is the energy of the state with wave function P. In Hartree atomic units (see the Preface) this equation becomes

$$-\frac{1}{2}\frac{d^2P}{dx^2} + V(x)P = EP \qquad (2)$$

or

$$P'' = 2(V(x) - E) P \qquad (3)$$

When $V(x) > E$ for both large, positive x and large, negative x, a discrete set of allowed energies occurs. This set occurs because, when $E > V(x)$, the wave function is oscillatory; this is the "classically allowed" region of space. When $E < V(x)$, the wave function decays toward zero; this is the "classically forbidden" region of space since, classically, when the total energy, E, of the particle is less than the potential energy, V(x), the kinetic energy of the particle must be negative. In classical physics, a negative kinetic energy, $\frac{1}{2}mv^2$, implies an imaginary velocity, v, which is the mathematical way of saying such motion cannot occur (in classical physics).

In quantum mechanics, the particle can spend some time in regions of space where $E < V(x)$. These are the classically forbidden regions outside the edges of a finite square well, for example. Quantum mechanical tunneling through barriers is also a result of this quantum mechanical penetration of classically forbidden regions of space.

Consider a region of space where $E < V(x)$ and where $V(x) \approx$ a constant V_0. The Schrödinger equation (3) becomes $P'' = 2(V_0 - E)P$. The two solutions to this equation (two because the equation is a second order differential equation) are $P \propto e^{\pm\alpha x}$ where $\alpha = \sqrt{2(V_0 - E)}$. If the region where $E < V(x)$ is bounded, both solutions can occur, but if the region is unbounded, then one of the two solutions is not allowed. If the region is unbounded towards $+\infty$, then $e^{+\alpha x}$ grows without bound; this implies that $|P|^2$ (the probability density for the particle) is arbitrarily large the farther out you go. Such an infinite probability of finding the particle at infinity is not allowed physically. Hence, the wave function must decay towards zero (in this case exponentially) as x becomes large. A similar argument holds for x tending toward $-\infty$; now it is the $e^{-\alpha x}$ term which diverges. The result is still that, as $|x|$ gets large, P tends to zero.

These demands on the wave function's behavior at large positive and negative x are the boundary conditions used both by the analytical methods of solution (those in which the solution is an equation for P) and by the numerical, computer-based methods presented in this booklet. Because the wave function must go smoothly to zero at large x, the particle can have only certain, discrete (i.e. separated from each other) total energies. As you will see, for other energies, the wave functions will not go to zero at large x.

P(x)

E < E$_0$

E = E$_0$

x

E > E$_0$

E$_0$ = an eigenvalue

P(x)

E > E$_0$

E = E$_0$

x

E < E$_0$
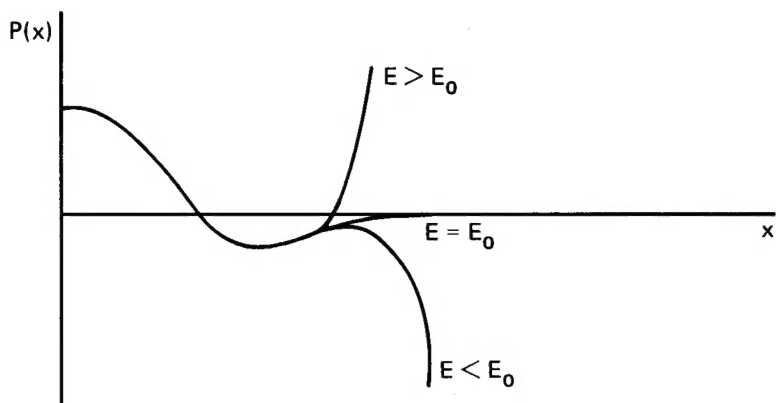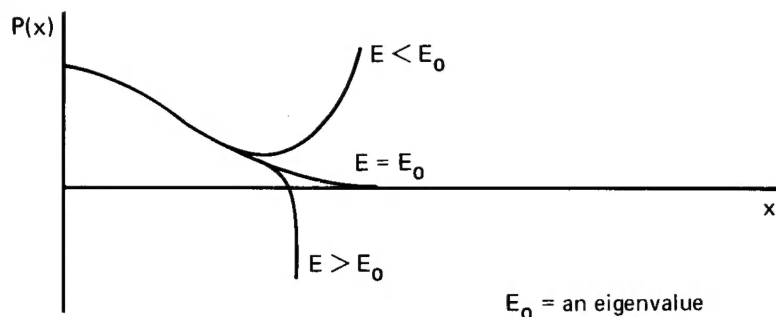
One of the big differences between analytical methods (leaving out approximate methods you learn in higher level quantum mechanics) and the method presented here is that analytical approaches can only solve five quantum mechanical problems (the infinite square well, the finite square well, the finite square barrier, the harmonic oscillator, and the hydrogen atom). The computer method can solve almost any Schrödinger equation problem for almost any potential, V. In this booklet we will limit ourselves to symmetric potentials since the vast majority of interesting potentials are symmetric (i.e. are such that $V(-x) = V(x)$).

THE COMPUTER APPROACH

The computer (or numerical) method is an "algorithmic" (or "iterative" or "step-by-step") method of solution. The computer approach integrates the Schrödinger equation by taking small steps, Δx, and finding the new values of the wave function, P, and its derivative, $P' = dP/dx$, after each little step.

Suppose you know the wave function, P, and its first derivative, P', at some point x. Suppose you also know how P should behave at some other x (for example, that P should go to zero as x gets large). Given any potential, $V(x)$, you try an energy, E; you set the initial values of P and P' at the point they are known; you take a small step Δx and calculate the new values of P and P' by using $P(x+\Delta x) = P(x) + P'(x+\Delta x/2)\Delta x$ and $P'(x+\Delta x) = P'(x) + P''(x+\Delta x/2)\Delta x$. Schrodinger's equation gives you the value of the second derivative, $P'' = d^2P/dx^2$. You now use the same procedure again to go from $x+\Delta x$ to the point $x+2\Delta x$, and so forth. In this way, you walk out x (integrating the Schrödinger equation step-by-step as you go) until you reach the other place at which you know the behavior of P. You then just look at the behavior of P; if E was one of the allowed energies (eigenvalues), then P will

behave correctly (e.g., P will go smoothly to zero for large x); if E was not a correct energy, then P will not behave (e.g., P will diverge for large x). If E is just more than an eigenvalue, P will diverge towards one infinity; if E is just below that eigenvalue, P will diverge to the other infinity. You can home in on eigenvalue energies quite quickly.

Figure 1 shows a block diagram (a simplified computer flow chart) for this procedure. One possible BASIC implementation of this procedure is:

```
10   DEF FNV(X)= ...... potential, V(x)
20   PRINT "END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?"
30   INPUT X9,X7,P,E  ⎫
40   LET P0=P1=X0=0   ⎪
50   LET X6=X9/20     ⎪
60   IF P=1 THEN 90   ⎬  Initialization
70   LET P0=1         ⎪
80   GOTO 100         ⎪
90   LET P1=1         ⎭
100  LET P2=2*(FNV(X0+X7/2)-E)*(P0+P1*X7/2)  ⎫  Integration of the
110  LET P0=P0+(P1+P2*X7/2)*X7               ⎬  Schrödinger equation
120  LET P1=P1+P2*X7                         ⎭
130  LET X0=X0+X7
140  IF X0<X6 THEN 170  ⎫
150  LET X6=X6+X9/20    ⎬  Print loop
160  PRINT X0,P0,P0*P0  ⎭
170  IF X0<X9 THEN 100 — Return for next Δx step
180  PRINT
190  GOTO 20 — Return for new parameters
200  END
```
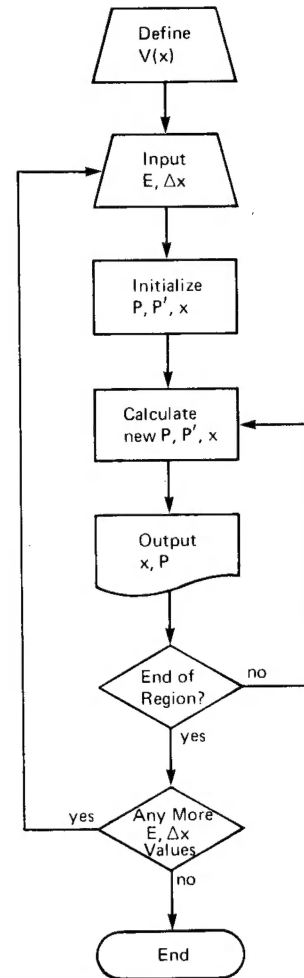

Figure 1. Flow Chart of Computer Approach One-Dimensional Quantum Mechanics

A few comments on the program are in order: First, there is no one "right" implementation of the procedure. Any program that calculates the quantities correctly is "right." The program shown is just one such correct implementation. Second, notice the use of the half-step method (see the Appendix) in the lines calculating $P2 = d^2P/dx^2$ from the Schrödinger equation and $P\emptyset =$ the wave function, P, from the first derivative, $P1 = dP/dx$. Third, the print-test lines are not necessary, but it is convenient not to print out on the terminal the results of all several hundred steps, Δx, you will be taking. Fourth, the potential, $V(x)$, is given as a defined function, $FNV(X)$, to emphasize that this short program solves any (symmetric potential) Schrödinger equation problem. All you do is type the potential into the DEF line. Finally, the initialization of $P\emptyset =$ the wave function and $P1 =$ the first derivative of the wave function with respect to x will be discussed in the next section.

INITIALIZATION

Much of upper level quantum mechanics hinges on the development of theorems concerning the Schrödinger equation (or its equivalents). One such theorem states:

> *The wave functions for the stationary states (i.e. the solutions of the time-independent Schrödinger equation) for a symmetric potential, $V(x)$, can always be written as completely even (i.e., $P(-x) = P(x)$) or completely odd (i.e., $P(-x) = -P(x)$).*

At first glance that theorem (which is proved in the Appendix for those of you with sufficient mathematical background) has little to do with our problem. In fact, the theorem gives our initial values of P and P' at $x = 0$. If P is to be even, then $P'(0)$ must be zero, and $P(0)$ cannot then be zero. If P is to be odd, then $P(0)$ must be zero, and $P'(0)$ cannot be zero. If both P and P' are zero anywhere, then, as you can see from the numerical procedure, P'', P', and P will be zero everywhere. The "correct" non-zero values for $P(0)$ (in the even case) or $P'(0)$ (in the odd case) would be given by the normalization condition $\int_{-\infty}^{\infty} |P|^2 dx = \int_{-\infty}^{\infty} P^2 dx = 1$. The easiest thing to do, however,

is to make $P(0) = 1$ (or $P'(0) = 1$), calculate the right shapes and energies for the states and, then, make the normalization correct. After all, as you can see from the Schrödinger equation, if P is a solution, then any constant times P is also a solution. We can normalize the wave function after we find it. This theorem has allowed us to set the initial values of P and P' at $x = 0$ and then integrate out to large x before examining the behavior to the tail of the wave function. There are other ways to start the procedure: that is, there are other ways to initialize P and P' at some known x. The procedure we're using works for all symmetric potentials.

THE HARMONIC OSCILLATOR

Let's work through a representative exercise. In fact, let's start with a problem that analytic methods can solve—the harmonic oscillator. The potential for a harmonic oscillator is $V(x) = kx^2/2$ where k is the so-called "spring constant." The prototype of a harmonic oscillator is a mass oscillating on a spring, but we're actually treating the problem of an electron in a potential proportional to x^2. For definiteness, let's set the spring constant, k, equal to 1, so that $V(x) = x^2/2$.

The harmonic oscillator can be solved analytically. The result is that the wave functions are Hermite polynomials and that the allowed energies are $E_n = (n+1/2)h\omega$ where $\omega = \sqrt{k/m}$. In atomic units $E_n = (n+1/2)\omega$ which means that, for our problem, $E_n = (n+1/2)$ or $E = .5, 1.5, 2.5, \ldots$ Each energy has a wave function that obeys the boundary conditions; no other energies

will work. Since these energies are known, we can check the numerical calculations by seeing if these energies work and others don't. Furthermore, if some other potential, V(x), looks sort-of like a harmonic oscillator potential, then these energies can also be used as first guesses at the energies for that potential.

SAMPLE SOLUTION

1. Plot the potential.

It's always a good idea to get a feeling for the potential the particle experiences. You can do this by a short program which prints out values which you then plot on graph paper. One such program (with its RUN for this problem) would be:

```
POTENT

10   FOR X0=0 TO 3 STEP .2
20   PRINT X0,X0*X0/2
30   NEXT X0
40   END

END

RUN
POTENT

0            0
.2           .02
.4           .08
.6           .18
.8           .32
1            .5
1.2          .72
1.4          .98
1.6          1.28
1.8          1.62
2            2
2.2          2.42
2.4          2.88
2.6          3.38
2.8          3.92
3.           4.5

END
```

You can also use the terminal plotting subroutines discussed in the Appendix. The program changes you write (and a RUN for this problem) could be:

```
5   READ X8,X9,Y8,Y9,Z8
6   DATA 8,3,8,5,1
7   GOSUB 9888
18  FOR X8=8 TO 3 STEP .2
18  LET Y8=X8*X8/2
28  GOSUB 9188
38  NEXT X8
35  GOSUB 9288
48  END

APPEND-TTYPLO
RUN
POTENT

MAX Y= 5
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX XXX
 Y
 Y
 Y
 Y                                                                    I
 Y
 Y
 Y                                                                  I
 Y
 Y
 Y
 Y
 Y                                                              I
 Y
 Y
 Y                                                          I
 Y
 Y
 Y                                                      I
 Y
 Y
 Y                                                  I
 Y
 Y
 Y                                              I
 Y
 Y
 Y                                          I
 Y
 Y                                      I
 Y
 Y                                  I
 Y
 Y                              I
 Y                          I
 Y                      I
 Y I      I      I
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
  MIN Y= 8   MIN X= 8                      MAX X= 3
```
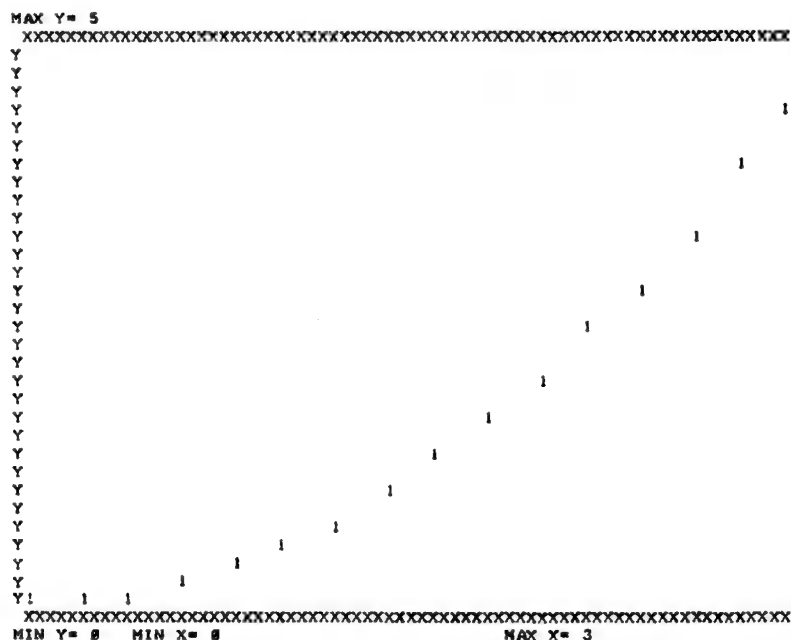
The potential is, of course, just a parabola. It is symmetric ($V(-x) = V(x)$) so we can use our computer approach as discussed above.

2.(a) Sketch the wave function for the lowest energy (the ground state) of the potential $V(x) = x^2/2$. Now find the wave function and energy of that state with the computer.

Let's use a program like that discussed above with the defined function for the potential. Then we just try different energies until the wave function behaves at large x. Large x usually means x several times the classical turning point (where $E = V(x)$); for this lowest state "large x" (the end of the interval of integration) can be 3 or 4.

Usually the lowest state for a symmetric potential is even; higher states usually alternate odd, even, odd, even, . . . A sensible expectation is to try for an even ground state. Notice, if the lowest state weren't even, the lowest odd state would just come out with a lower energy. The program and a RUN look like:

```
IDSCHR

10  DEF FNV(X)=X*X/2 —Potential, V(x)
20  PRINT "END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?"
30  INPUT X9,X7,P,E
40  LET P0=P1=X0=0
50  LET X6=X9/20
60  IF P=1 THEN 90            Initialization
70  LET P0=1
80  GOTO 100
90  LET P1=1
100 LET P2=2*(FNV(X0+X7/2)-E)*(P0+P1*X7/2)
110 LET P0=P0+(P1+P2*X7/2)*X7       Integration of the
120 LET P1=P1+P2*X7                  Schrödinger equation
130 LET X0=X0+X7
140 IF X0<X6 THEN 170
150 LET X6=X6+X9/20         Print loop
160 PRINT X0,P0,P0*P0
170 IF X0<X9 THEN 100 —Return for next Δx
180 PRINT
190 GOTO 20 —Return for new parameters
200 END

RUN
IDSCHR

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?3,.01,0,.45
 .15          .989934       .979969
 .31          .95782        .917419
 .46          .989852       .82783
 .61          .847857       .718861
 .76          .775826       .601986
 .989999      .698172       .487445
1.06          .619367       .383615
1.21          .543639       .295544
1.36          .474765       .225402
1.51          .416995       .173052
1.66          .378122       .13699
1.81          .339714       .115486
1.96          .327534       .107279
2.1           .33576        .112735
2.25          .370073       .137326
2.40001       .44053        .194067
2.55001       .559386       .312913
2.70001       .749964       .562476
2.85002       1.05051       1.10356
3.00002       1.52538       2.32678

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?3,.01,0,.55
 .15          .987692       .975536
 .31          .94836        .899386
 .46          .889394       .791021
 .61          .812719       .660512
 .76          .722762       .522385
 .989999      .624298       .389748
1.06          .521966       .272449
1.21          .419833       .17626
1.36          .32104        .103066
1.51          .227548       5.17781E-02
1.66          .139977       1.95935E-02
1.81          5.74888E-02   3.30497E-03
1.96          -2.23332E-02  4.98771E-04
2.1           -9.81286E-02  9.62922E-03
2.25          -.186798      3.48935E-02
2.40001       -.292506      8.55596E-02
2.55001       -.429501      .184471
2.70001       -.619735      .384071
2.85002       -.898043      .806481
3.00002       -1.32131      1.74585

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?3,.01,0,.5
 .15          .988813       .977751
 .31          .953086       .908373
 .46          .899605       .809288
 .61          .838232       .689265
 .76          .749162       .561244
 .989999      .660968       .436878
1.06          .570181       .325107
1.21          .480921       .231285
1.36          .396689       .157299
1.51          .319801       .102272
1.66          .252129       6.35691E-02
1.81          .194353       3.77732E-02
1.96          .146482       .021457
2.1           .11824        1.21528E-02
2.25          .079544       6.32724E-03
2.40001       5.61128E-02   3.14865E-03
2.55001       3.86947E-02   1.49728E-03
2.70001       2.60771E-02   6.80016E-04
2.85002       1.71633E-02   2.94579E-04
3.00002       1.10143E-02   1.21314E-04

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?
END
```

As we expected, the energy of the state is near .5. You can get higher accuracy by using a smaller step size (Δx), but because the computer keeps numbers to only finite accuracy and because the calculational method is not perfectly accurate, the computer may not give you exactly .5 as an answer. The difference from .5 is a measure of the accuracy of the method.

2.(b) In which regions of x is the probability of finding the particle nearly zero? In which regions of x is the probability of finding the particle relatively large?

Since P is real, $|P|^2 = P^2$. By looking at the printout you can see there is one loop (or anti-node) in P^2 and there are no nodes. The probability is near zero only for large positive and large negative x. The probability is large near $x = 0$. You can also plot the wave function and its square on the terminal. The changes you make and the RUN are:

```
5 LET X8=Y8=0
6 LET Y9=1
35 GOSUB 9000
160 LET Z0=1
162 LET Y8=P0
163 GOSUB 9100

164 LET Z0=2
165 LET Y0=P0*P0
166 GOSUB 9100
180 GOSUB 9200
APPEND-TTYPLO
RUN
1DSCHR

END OF INTERVAL, DELTA-X, PARITY (0=EVEN, 1=ODD), ENERGY?
?3,.81,0,.5
MAX Y= 1
```



```
END OF INTERVAL, DELTA-X, PARITY (0=EVEN, 1=ODD), ENERGY?
?
END
```

2.(c) *Find the normalization constant for the wave function of this state.*

To normalize a wave function, you calculate $A = \int_{-\infty}^{\infty} |P|^2 dx$. Since

$P(x)$ is real, $|P|^2 = P^2$. The normalization constant (i.e., the number

you multiply P by everywhere) is then $1/\sqrt{A}$. The total integral $\int_{-\infty}^{\infty}$

$P^2 dx$ is just twice the sum of $P^2 \Delta x$ from $x = 0$ to your end of interval.
Thus, with a minor change in your wave function program, you can
calculate A directly.

```
45 LET P3=0
115 LET P3=P3+P0*P0*X7
160 PRINT X0,P0,P0*P0,P3
RUN
1DSCHR

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?3,.01,0,.5
 .15             .988813         .977751          .148769
 .31             .953086         .908373          .299887
 .46             .899605         .809288          .428555
 .61             .839232         .689285          .540528
 .76             .749162         .561244          .633699
 .909999         .668968         .436878          .707828
1.06             .570181         .325107          .764219
1.21             .480921         .231285          .805237
1.36             .396609         .157299          .833765
1.51             .319801         .102272          .852735
1.66             .252129         6.35691E-02      .864797
1.81             .194353         3.77732E-02      .87213
1.96             .146482         .021457          .876393
2.1              .11024          1.21528E-02      .878645
2.25             .079544         6.32724E-03      .87996
2.40001          5.61128E-02     3.14865E-03      .88063
2.55001          3.86947E-02     1.49728E-03      .880957
2.70001          2.60771E-02     6.80016E-04      .881109
2.85002          1.71633E-02     2.94579E-04      .881176
3.00002          1.10143E-02     1.21314E-04      .881204
```

The normalization constant is $1/\sqrt{2(.881)} = .753$.

2.(d) *Find the position x_0 such that the probability of finding the particle
between $-x_0$ and $+x_0$ is 1/2.*

What you really want is the x_0 such that $\int_{-x_0}^{x_0} |P|^2 dx = 1/2$ when P is

normalized. All you need to do is look down the printout from Part 2(c)
to find the point where the sum of $P^2 \Delta x = A/2$. The point is very near
$x = .47$ atomic units $= .150$ Å. (For higher accuracy you could change
the print-test so values are printed more often on the terminal. You
might also plot the $P^2 \Delta x$ function and estimate the point x_0 graphically.)

3.(a) *Sketch the wave function for the second lowest energy of $V(x) = x^2/2$.
Now find the energy and wave function for this state with the computer.*

3.(b) *In which regions of x is the probability of finding the particle nearly zero?
In which regions of x is the probability of finding the particle relatively large?*

3.(c) *Find the normalization constant for this state.*

3.(d) *Find the position such that the probability of finding the particle between* $-x_0$ *and* $+x_0$ *is 1/2.*

The RUNs for this part of the problem follow:

```
IDSCHR

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?4,.01,1,1.48
 .21          .205476        4.22204E-02
 .41          .377375        .142412
 .61          .587786        .257846
 .809999      .586386        .343848
1.01          .611624        .374084
1.21          .58987         .347947
1.41          .53382         .284111
1.61          .455398        .207388
1.81          .37085         .13753
2.01          .298693        8.45822E-02
2.2           .225835        5.18815E-02
2.40001       .174084        3.02774E-02
2.60001       .141619        .020056
2.80002       .138921        1.71403E-02
3.00002       .146246        2.13878E-02
3.20003       .197919        3.91718E-02
3.40003       .309367        9.57079E-02
3.60003       .531873        .282889
3.80004       .977555        .955614
4.00004      1.89648         3.59665

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?4,.01,1,1.52
 .21          .205354        4.21703E-02
 .41          .376581        .141753
 .61          .585072        .255897
 .809999      .580517        .337
1.01          .601299        .361561
1.21          .57397         .329441
1.41          .51065         .260763
1.61          .425769        .181279
1.81          .332998        .110888
2.01          .243017        5.90574E-02
2.2           .166152        2.76065E-02
2.40001       9.66091E-02    9.33332E-03
2.60001       3.72868E-02    1.39031E-03
2.80002      -1.67988E-02    2.82199E-04
3.00002      -7.45786E-02    5.56196E-03
3.20003      -.151041        2.28133E-02
3.40003      -.272922        7.44567E-02
3.60003      -.492861        .242124
3.80004      -.916188        .839253
4.00004      -1.78054        3.17033

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?4,.01,1,1.5
 .21          .205415        4.21953E-02
 .41          .376936        .142082
 .61          .586427        .256469
 .809999      .583447        .340411
1.01          .60645         .367782
1.21          .581894        .338691
1.41          .521783        .272257
1.61          .44040         .194031
1.81          .351766        .123739
2.01          .2666          7.10753E-02
2.2           .1956          3.82595E-02
2.40001       .134691        1.81416E-02
2.60001       8.84811E-02    7.82890E-03
2.80002       .055496        3.07981E-03
3.00002       .033239        1.10463E-03
3.20003       .018984        3.60393E-04
3.40003       1.02688E-02    1.05449E-04
3.60003       5.11185E-03    2.61310E-05
3.80004       2.02241E-03    4.09612E-06
4.00004      -1.31169E-04    1.72054E-06

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?
END
```

To plot the functions, start again with the basic program and add:

```
5 READ X8,Y8,Y9
6 DATA 8,8,1
35 GOSUB 9888
168 LET Z8=1
161 LET T8=P8
162 GOSUB 9188
163 LET Z8=2
164 LET Y8=P8*P8
165 GOSUB 9188
188 GOSUB 9288
APPEND-TTYPLO
RUN
IDSCHR

END OF INTERVAL, DELTA-X, PARITY (8=EVEN; 1=ODD), ENERGY?
?4,.81,1,1.5
MAX Y= 1
```


Note: Curve 1 is wave function x = 0 to x = 4; curve 2 is the square of the wave function.

3.(e) How many nodes are there in $[P(x)]^2$?

There are 2 loops and 1 node between $-\infty$ and $+\infty$. The rule of thumb is that the lowest energy state has 0 nodes, the next state has 1 node, etc. The probability is nearly zero around $x = 0$ and for large positive and negative x. The probability is large near $x = +1$ and $x = -1$.

3.(f) Find the normalization constant.

3.(g) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

Starting again from the basic program, add:

```
45 LET P3=0
115 LET P3=P3+P8*P8*X7 — adds up P² △x
168 PRINT X8,P8,P8*P8,P3
RUN
IDSCHR

END OF INTERVAL, DELTA-X, PARITY (8=EVEN; 1=ODD), ENERGY?
?4,.81,1,1.5
 .21        .285415         4.21953E-82     3.22862E-83
 .41        .376938         .142882         2.15839E-82
 .61        .586427         .256469         6.28956E-82
 .889999    .583447         .348411         .123885
 1.81       .68645          .367782         .194978
 1.21       .581894         .338681         .266289
 1.41       .521783         .272257         .327448
 1.61       .44849          .194831         .37369
 1.81       .351766         .123739         .484872
 2.81       .2666           7.18753E-82     .423768
 2.2        .1956           3.82595E-82     .433746
 2.48881    .134691         1.81416E-82     .439881
 2.68881    8.84811E-82     7.82898E-83     .441583
 2.88882    .855496         3.87981E-83     .442585
 3.88882    .833239         1.18483E-83     .442883
 3.28883    .816984         3.68393E-84     .443814
 3.48883    1.82688E-82     1.85449E-84     .443854
 3.68883    5.11185E-83     2.61318E-85     .443866
 3.88884    2.82241E-83     4.89812E-86     .443868
 4.88884    -1.31169E-84    1.72854E-88     .443868
```

The normalization constant is $1/\sqrt{2(.443)} = 1.062$. The point at which the sum of $P^2\Delta x = .221$ is approximately $x = 1.1$ atomic unit $= .532$ Å.

4. Find the difference in energy between these states in eV, Hertz, and Å.

E = 1 atomic unit = 27.210; eV = 6.58 x 10^{15} Hertz; lambda = 456 Å. (Using 1 eV = 1.602 x 10^{-12} ergs; h = 6.624 x 10^{-27} erg-sec; c = 2.998 x 10^{10} cm/sec)

5.(a) Find the behavior of each state near x = 0.

Consider $\ln(P(0)-P)$ versus $\ln(x)$ for small x. What is the power dependence of P for small x?

The slope of a straight line on a log-log plot is the power, B, to which x is raised in $(P(0)-P) \sim x^B$. You may want to plot your results on graph paper although you can calculate the result directly from printout.

Starting again from the basic program:

```
GET-1DSCHR
140
150
160 PRINT LOG(X0),LOG(1-P0)
170 IF X0<.1 THEN 100
RUN
1DSCHR

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?3,.01,0,.5
-4.60517      -9.90451
-3.91202      -8.51762
-3.50656      -7.70676
-3.21888      -7.13148
-2.99573      -6.68535
-2.61341      -6.32093
-2.65926      -6.01294
-2.52573      -5.74623
-2.40795      -5.51107
-2.30259      -5.30083

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?
END
```

So this wave function comes off of its value at x = 0 (P(0)=1) quadratically. The normalization doesn't change this fact. The first exicted state (the second one found above) comes out of P(0) = 0 linearly in x. Any even state must come off its x = 0 value as an even power of x; any odd state must start out from x = 0 as an odd power of x.

You actually know a good deal about a wave function before you start a problem. Often the Schrödinger equation can be approximated in some regions of space by an equation with known solutions. The idea of these asymptotic solutions for small and large x will be important again in Chapter two.

5.(b) Find the behavior of each state for large x.

Consider $\ln(P)$ versus x for large x. Is the dependence of the wave function beyond the classical turning point faster than $e^{-\alpha x}$ where α is some constant?

If the potential became a constant, V0, for large enough x, the tail of the wave function would approach $\exp(-\alpha x)$ where $\alpha = \sqrt{2(V0-E)}$. Many potentials do approach constant values, but $V(x) = x^2/2$ clearly approaches infinity. So, you expect the wave function to tail off to zero faster than exponentially. You may want to plot the results on graph paper.

Starting again from the basic program, change:

```
140 IF X0<2.9 THEN 170
160 PRINT X0,LOG(P0)
RUN
IDSCHR

END OF INTERVAL, DELTA-X, PARITY (0=EVEN; 1=ODD), ENERGY?
?3,.01,0,.5
   2.90002        -4.2099
   2.91002        -4.23922
   2.92002        -4.26867
   2.93002        -4.29823
   2.94002        -4.32791
   2.95002        -4.35771
   2.96002        -4.38763
   2.97002        -4.41768
   2.98002        -4.44785
   2.99002        -4.47814
   3.00002        -4.50856
```

So the tail of the wave function falls off faster than exponentially because $V(x)$ is still rising fast. The normalization doesn't affect this result either. Interestingly, if you assume that the tail behaves as $\exp(-(\alpha(x)x)$ where $\alpha(x) = \sqrt{2(V(x)-E)}$, you can get good agreement with the asymptotic behavior of P at large x.

EXERCISES — Use computer when appropriate

I. For the potential $V(x) = x^2$:

1. Plot the potential for $0 <= x <= 5$.

2.(a) Find the ground state energy and wave function.

2.(b) How many nodes are there in $[P(x)]^2$?

2.(c) Find the normalization constant.

2.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

3.(a) Find the first excited state wave function and energy.

3.(b) How many nodes are there in $[P(x)]^2$?

3.(c) Find the normalization constant.

3.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

4. Calculate the energy difference between these two lowest states, ΔE, in atomic units, eV, Hertz, and Å.

5.(a) Find the behavior of each state near x = 0.

5.(b) Find the behavior of each state for large x.

Hint: The energies are known from the harmonic oscillator with k = 2.

II. For the potential $V(x) = (x^2/2) + 4 \exp(-x^2)$, which is a harmonic oscillator with a Gaussian bump in the center (a model of the potential of the nitrogen atom in an ammonia molecule):

1. Plot the potential for $0 <= x <= 5$.

2.(a) Find the ground state energy and wave function.

2.(b) How many nodes are there in $[P(x)]^2$?

2.(c) Find the normalization constant.

2.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

3.(a) Find the first excited state wave function and energy.

3.(b) How many nodes are there in $[P(x)]^2$?

3.(c) Find the normalization constant.

3.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

4. Calculate the energy difference, ΔE, between these two lowest states in eV, Hertz, and Å.

5.(a) Find the behavior of each state near $x = 0$.

5.(b) Find the behavior of each state for large x.

6. Compare the energies and wave functions of these two states to those discussed in the chapter (i.e., the two lowest energy states for the harmonic oscillator $x^2/2$).

Hint: Use the proper harmonic oscillator energies as first guesses and then hunt.

III. For the potential $V(x) = 16x^2/(x^2+16)$ which starts out as a harmonic oscillator but then becomes constant for $x \gg 4'$.

1. Plot the potential for $0 <= x <= 5$.

2.(a) Find the ground state energy and wave function.

2.(b) How many nodes are there in $[P(x)]^2$?

2.(c) Find the normalization constant.

2.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

3.(a) Find the first excited state wave function and energy.

3.(b) How many noises are there in $[P(x)]^2$?

3.(c) Find the normalization constant.

3.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

4. Calculate the energy difference, ΔE, between these two lowest states in eV, Hertz, and Å.

5.(a) Find the behavior of each state near $x = 0$.

5.(b) Find the behavior of each state for large x.

6. Compare the energies and wave functions of these two states to those discussed in the chapter (i.e., the two lowest energy states for the harmonic oscillator $x^2/2$.)

Hint: Use the proper harmonic oscillator energies as first guesses and then hunt.

IV. For the potential $V(x) = -10 \exp(-x^2/2)$, which is a Gaussian well:

    1. Plot the potential for $0 < = x = < = 5$.

    2.(a) Find the ground state energy and wave function.

    2.(b) How many nodes are there in $[P(x)]^2$?

    2.(c) Find the normalization constant.

    2.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is $1/2$.

    3.(a) Find the first excited state wave function and energy.

    3.(b) How many nodes are there in $[P(x)]^2$?

    3.(c) Find the normalization constant.

    3.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is $1/2$.

    4. Calculate the energy difference, ΔE, between these two lowest states in eV, Hertz, and Å.

    5.(a) Find the behavior of each state near $x = 0$.

    5.(b) Find the behavior of each state for large x.

    6. Compare the energies and wave functions of these two states to those discussed in the chapter (i.e., the two lowest energy states for the harmonic oscillator $x^2/2$).

    Hint: Use the proper harmonic oscillator energies as first guesses and then hunt.

*V. For the potential $V(x) = -\exp(-|x|/10)/|x|$, which is the one-dimensional equivalent of the screened Coulomb potential (important in many electron atoms):

    1. Plot the potential for $0 < x < = 5$.

    2.(a) Find the ground state energy and wave function.

    2.(b) How many nodes are there in $[P(x)]^2$?

    2.(c) Find the normalization constant.

    2.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is $1/2$.

    3.(a) Find the first excited state wave function and energy.

    3.(b) How many nodes are there in $[P(x)]^2$?

    3.(c) Find the normalization constant.

    3.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is $1/2$.

    4. Calculate the energy difference, ΔE, between these two lowest states in eV, Hertz, and Å.

5.(a) Find the behavior of each state near x = 0.

5.(b) Find the behavior of each state for large x.

Hint: Because the potential is infinite at x = 0, only odd states are allowed. The (unscreened) Coulomb potential (the hydrogen atom) energies for these states are -.5 and -.125; you will find both energies moved up. This potential is important in three dimensional quantum mechanics (Chapter Two). There, it turns out, the wave function is R(r) = P(r)/r where P(r) is the wave function you derive in this problem. You might look at the behavior of P(r)/r in your printout.

VI. For the potential $V(x) = (|x|-1)^2/2$, the biharmonic oscillator:

1. Plot the potential for $0 <= x <= 5$.

2.(a) Find the ground state energy and wave function.

2.(b) How many nodes are there in $[P(x)]^2$?

2.(c) Find the normalization constant.

2.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

3.(a) Find the 4th excited state wave function and energy.

3.(b) How many nodes are there in $[P(x)]^2$?

3.(c) Find the normalization constant.

3.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

4. Calculate the energy difference, ΔE, between these two lowest states in eV, Hertz, and Å.

5.(a) Find the behavior of each state near x = 0.

5.(b) Find the behavior of each state for large x.

6. Compare the energies and wave functions of these two states to those discussed in the chapter (i.e., the two lowest energy states for the harmonic oscillator $x^2/2$).

Hint:Use the proper harmonic oscillator energies as first guesses and then hunt.

VII. For the potential $V(x) = x^2/2$:

1. Plot the potential for $0 <= x <= 5$.

2.(a) Find the 3rd excited state (the fourth state) energy and wave function.

2.(b) How many nodes are there in $[P(x)]^2$?

2.(c) Find the normalization constant.

2.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

3.(a) Find the 4th excited state wave function and energy.

3.(b) How many nodes are there in $[P(x)]^2$?

3.(c) Find the normalization constant.

3.(d) Find the point x_0 such that the probability of finding the particle between $-x_0$ and x_0 is 1/2.

4. Calculate the energy difference, ΔE, between these two lowest states in eV, Hertz, and Å.

5.(a) Find the behavior of each state near $x = 0$.

5.(b) Find the behavior of each state for large x.

6. Compare the energies and wave functions of these two states to those discussed in the chapter (i.e., the two lowest energy states for the harmonic oscillator $x^2/2$).

Hint: Use the proper harmonic oscillator energies as first guesses and then hunt.

**VIII. The family of potentials, $V(x) = |x|^m$ for different integers, m. form an interesting progression, the $m = 2$ member is a harmonic oscillator with energies, $E_n = (n + 1/2)\sqrt{2}$; the limit as $m \to \infty$ is the infinite square well.

1. Find the wave functions and energies for the ground state with $m = 2$, 4, 6, 8, and 10.

2. Find the wave functions and energies for the first excited state with $m = 2, 4, 6, 8,$ and 10.

3. Plot the energies as functions of the power, m.

4. Interpret the shapes of the curves from Part 3.

**IX. For the potential $V(x) = (-x^2/2) + A \exp(-x^2)$:

1. Find the energies and wave functions of the ground and first excited states as functions of the height, A, of the Gaussian bump.

2. Plot the energies and their difference versus the height of the bump.

3. Explain the changes in shapes of the wave functions. What conclusions can you draw about the energies? Consider the extrapolations to $A = 0$ and $A = \infty$; consider the relationship of the kinetic and potential energy terms in the Schrödinger equation.

CHAPTER TWO: THREE-DIMENSIONAL BOUND STATES

INTRODUCTION

In general, three-dimensional quantum mechanics is thought to be much more difficult than the one-dimensional case. For spherically symmetric potentials, the computer makes three-dimensional quantum mechanics just as easy as one-dimensional.

The three-dimensional time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r}) \tag{4}$$

where ψ is the wave function for the energy E and $V(\vec{r})$ is the potential. In polar coordinates (r, θ, ϕ) this equation becomes

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right] - \frac{\hbar^2}{2mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] \tag{5}$$

$$+ V(r, \theta, \phi)\psi = E\psi$$

If $V(r, \theta, \phi)$ is spherically symmetric, i.e., $V(\vec{r}) = V(r)$, then Equation (5) separates in polar coordinates. The wave function can be written as $\psi = R(r)Y(\theta, \phi)$. You substitute this product in for ψ, put all the terms containing $R(r)$ on one side and all those containing $Y(\theta, \phi)$ on the other; then set both sides equal to a constant ($\ell(\ell+1)$ where ℓ is any integer that is convenient). This provides the following equations for $R(r)$ and $Y(\theta, \phi)$:

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right] + \left[V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]R(r) = ER(r) \tag{6}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\theta^2}\right] + \ell(\ell+1)\ Y(\theta,\phi) = 0 \tag{7}$$

THE EQUATIONS IN θ and ϕ

The equation for Y can be separated again as $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$ with the result that

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\ell(\ell+1) - \frac{m^2}{\sin^2\theta}\right)\theta = 0 \tag{8}$$

$$\frac{d^2\Phi}{d\theta^2} + m^2\Phi = 0 \tag{9}$$

The $\Phi(\phi)$ equation has the solutions

$$\Phi(\phi) = e^{-im\phi} \text{ and } e^{+im\phi} \tag{10}$$

where m is an integer such that $|m| <= \ell$. Since we will only use Φ in applications involving $|\psi|^2$ for the $\phi = 0 - \phi = 180°$ plane, we don't have to worry about Φ at all. If you need to use Φ, you can call the SIN( ) and COS( ) functions on the computer.

The equations for $\Theta(\theta)$ is the associated Legendre equation; its solutions are known as associated Legendre polynomials, $\mathcal{L}_\ell^m$, so

$$\Theta(\theta) = \mathcal{L}_\ell^m (\cos\theta) \tag{11}$$

The other solution to this second order differential equation for θ isn't finite throughout the range of θ and so is not allowed to occur in most physics problems. So the solution for the angular parts of the full wave function, ψ, is

$$Y(\theta,\phi) = N_{\ell m}\mathcal{L}_\ell^m (\cos\theta) e^{\pm im\phi} \tag{12}$$

where $N_{\ell m}$ is just a normalization constant.

You can calculate values for $\Theta(\theta)$ and $\Phi(\phi)$ easily on the computer. To calculate Θ you could integrate the differential equation numerically. However, like sines and cosines, associated Legendre polynomials are well known and can be looked up in books. The first few angular wave functions, $Y_\ell^m (\theta, \phi)$ are

$$Y_0^0 = 1/\sqrt{4\pi}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \ , \ \ Y_1^1 = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{+im\phi} \ , \ \ Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-im\phi}$$

One possible program to calculate the Y_ℓ^m s is the following:

```
YLM

 10   PRINT "L (0 OR 1), M (/M/<=L)?"
 20   INPUT L,M
 30   LET P1=3.14159
 40   LET N0=1/SQR(4*P1)    ⎫
 50   LET N1=SQR(3/(4*P1))  ⎬  Useful constants for calculation
 60   LET N2=SQR(3/(8*P1))  ⎭
 70   FOR T1=0 TO P1 STEP P1/6 ◄——— Step across θ
 80   LET C1=COS(T1)
 90   LET S1=SIN(T1)
100   PRINT "THETA =";180*T1/P1
110   FOR T2=0 TO 2*P1 STEP 2*P1/6 ◄——— Step across φ
120   PRINT 180*T2/P1,
130   IF L>0 THEN 160  ⎫
140   PRINT N0          ⎬  Y₀⁰
150   GOTO 230          ⎭
160   IF M <> 0 THEN 190 ⎫
170   PRINT N1*C1         ⎬  Y₁⁰
180   GOTO 230            ⎭
190   IF M=1 THEN 220
200   PRINT N2*S1*COS(T2),N2*S1*SIN(T2) ⎫ Y₁¹
210   GOTO 230                          ⎭
220   PRINT N2*S1*COS(T2),-N2*S1*SIN(T2) ◄—— Y₁⁻¹
230   NEXT T2 ◄— φ
240   PRINT
250   NEXT T1 ◄— θ
260   PRINT
270   GOTO 10 ◄——— Return for new parameters
280   END
```

THE RADIAL EQUATION

The real problem of three-dimensional, spherically-symmetric-potential, quantum mechanics is to solve the radial wave equation, equation (6). Only one problem (the hydrogen atom, which is the unscreened Coulomb potential) can be solved analytically. All other problems need approximate methods of one sort or another (perturbation theory or variational methods), and sooner or later even these approximate methods need a computer.

Using the computer, an entirely different approach can be taken. You can integrate iteratively to find the radial wave function and the energy. Such a procedure can be carried out for any potential, $V(r)$. Just as was true in Chapter One on one-dimensional bound states, the computer approach for three-dimensional bound states is easy to understand but very general.

First, we reduce the three-dimensional radial wave equation to one that looks just like the one-dimensional Schrödinger equation discussed in Chapter One. Let $P(r) = rR(r)$. You then plug $P(r)$ into the radial wave equation (6) and find the equation $P(r)$ satisfies. The result is

$$-\frac{h^2}{2m}\frac{d^2P(r)}{dr^2} + \left[V(r) + \frac{h^2\ell(\ell+1)}{2mr^2}\right]P(r) = EP(r) \qquad (13)$$

In atomic units (for which $h=m=e=1$; see the Preface) this equation becomes

$$-\frac{1}{2}\frac{d^2P(r)}{dr^2} + \left[V(r) + \frac{\ell(\ell+1)}{2r^2}\right]P(r) = EP(r) \qquad (14)$$

or

$$P'' = 2\left[V(r) + \frac{\ell(\ell+1)}{2r^2} - E\right]P \qquad (15)$$

This last equation looks just like the one-dimensional Schrödinger equation discussed in Chapter One. The only differences are (1) that you are integrating with respect to r instead of x (so, for example, the range of r is 0 to $+\infty$) and (2) that the potential $V(x)$ is replaced by the effective potential $V_{eff}(r) \equiv V(r) + \frac{\ell(\ell+1)}{2r^2}$. We can solve this equation just as we did the one-dimensional Schrödinger equation.

Suppose you know the reduced radial wave function, $P(r)$, and its first derivative, $P'(r) = \frac{dP}{dr}$, at some point r_1. Suppose you also know the behavior of P somewhere else (for example, (1) that $P(r)$ must go smoothly to zero as r approaches zero (because $R(r)$ must remain bounded)). Then, for any potential, $V(r)$, you can choose an energy E, set $P(r)$ and $P'(r)$ at that first point r_1, integrate from r_1 to the second region, and examine $P(r)$. If the energy you chose was an eigenvalue (one of the allowed energies for the system), then $P(r)$ (and $R(r)$) will behave correctly. If E was not an eigenvalue, $P(r)$ will diverge. The divergence will be to opposite infinities on opposite sides of an eigenvalue.

Using a computer, the integration can be performed in a step-wise way. Knowing $P(r)$ and $P'(r)$ at some point r, you find the values at $r+\Delta r$ from

$$P(r+\Delta r) = P(r) + P'(r+\frac{\Delta r}{2})\Delta r \qquad (16)$$

$$P'(r+\Delta r) = P'(r) + P''(r+\frac{\Delta r}{2})\Delta r \qquad (17)$$

d^2P/dr^2 can be calculated from the radial wave equation for P. The derivatives are evaluated in the middle of each interval $[r, r+\Delta r]$ so that the calculations are more accurate (see the Appendix).

Figure 2 shows a simplified flow chart for the strategy of the computer calculation. Before we can discuss an implementation of this strategy, we must discuss the initialization of P and P' further.
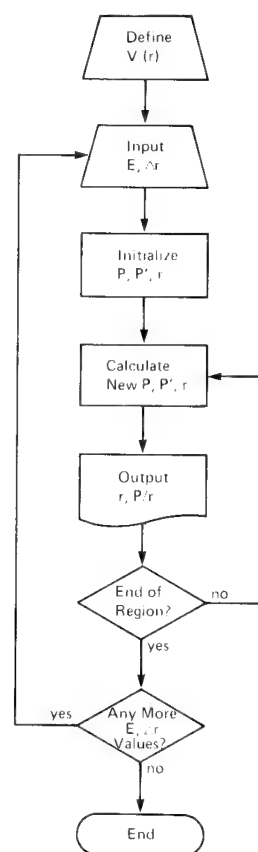
Figure 2. Flow Chart of Computer Approach Three-Dimensional Quantum Mechanics

INITIALIZATION

There are a number of ways to initialize $P(r)$ and $P'(r)$. Two ways are most common: the first initializes the (reduced) wave function, P, and its derivative at large r (and then observes the behavior at small r); the second initializes the (reduced) wave function, P, and its derivative at small r (and then observes the tail at large r). Large r in these contexts means several times the classical turning radius (where the effective potential equals the chosen energy). Both methods involve asymptotic expansions of the wave function for some values of r. We'll discuss each method in turn.

The first method expands the (reduced) wave function, P, and its derivative, P', for large r. If the potential is such that, beyond some point, r_0, the variation of the effective potential is negligible, then $V(r) + \frac{\ell(\ell+1)}{2r^2}$ is a constant, say V_0. The Schrödinger equation for P takes on its asymptotic form

$$P'' = 2(V_0 - E)P \tag{18}$$

whose solutions are $\exp(-ar)$ and $\exp(+ar)$ where $a = \sqrt{2(V_0 - E)}$. Because there must not be infinite probability of finding the particle at infinity, the solution e^{+ar} is not allowed. The result is that, beyond the point r_0, $P(r) \approx \exp(-ar)$ and therefore $P'(r) \approx -a \exp(-ar)$. You can initialize P and P' far enough out in r and then integrate step-by-step back towards $r = 0$. The boundary condition imposed then at $r = 0$ is that $R(r)$ must be bounded (hence $P(r)$ must go to zero smoothly). Again the reason for this boundary condition is that infinite probabilities are not allowed physically. When you use this strategy, you will have to watch the behavior of $P(r)$ and $R(r) = P(r)/r$ carefully very near the origin $(r = 0)$. An implementation of the program using this initialization might look like:

```
10   DEF FNV(R)=400*(R↑(-12)-R↑(-6))—Potential, V(r)
20   PRINT "R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?"
30   INPUT R9,R8,R7,L,E
40   LET R7=-ABS(R7)
50   LET P0=EXP(-SQR(2*(FNV(R9)-E))*R9)
60   LET P1=-SQR(2*(FNV(R9)-E))*P0      Initialization at large r
70   LET R=R9
80   PRINT R,P0,P0/R
90   LET R5=(R8-R9)/20
100  LET R6=R+R7/2
110  LET P2=2*(FNV(R6)+L*(L+1)/(2*R6*R6)-E)*(P0+P1*R7/2)   Integration of
120  LET P0=P0+(P1+P2*R7/2)*R7                              the Schrödinger
130  LET P1=P1+P2*R7                                        equation
140  LET R=R+R7
150  IF R>R5 THEN 180
160  LET R5=R5+(R8-R9)/20   Print loop
170  PRINT R,P0,P0/R
180  IF R>R8 THEN 100—Return for next Δr
190  PRINT
200  GOTO 20— Return for new parameters
210  END
```

The second method of initialization uses expansions of the reduced wave function, $P(r)$, near the origin. Sometimes the Schrödinger equation reduces to a simple form for small r; sometimes the solution near the origin reduces to a solution already known. In either of these cases this second method of initialization is the easier to use. A common example is the screened Coulomb potential, $-\exp(-r/r_0)/r$. This potential is a good approximation to the potential experienced by the electrons in many electron atoms. For small r, this potential reduces to the unscreened Coulomb potential, $-1/r$. The analytic solution for the hydrogen atom (the unscreened Coulomb potential) can be expanded for small r, as $R(r) \approx r^{\ell}$. So the small r behavior of the wave function for any potential which reduces to $-1/r$ for small r (in particular for the screened Coulomb potential) is given by:

$$P(r) \sim r^{\ell+1} \tag{19}$$

so that

$$P'(r) \sim (\ell+1)r^{\ell} \tag{20}$$

In this method of initialization, you set P and P' near $r=0$ and then integrate step-wise out to large r. At large r, if the energy, E, you chose was an allowed energy (an eigenvalue), the reduced wave function, P, will go smoothly to zero as will, therefore, the radial wave function $R(r) = P(r)/r$. (This is the behavior of P and P' whenever $V(r)$ is dominated by the angular momentum term $\ell(\ell+1)/(2r^2)$ for small r. The asymptotic equation for small r is then $P'' = \dfrac{\ell(\ell+1)}{r^2} P$ which has the solution $P = r^{\ell+1}$.)

A SCREENED COULOMB POTENTIAL PROGRAM

One implementation of this computer strategy, based on initialization by expansion for small r, is shown below. The potential is a screened Coulomb potential which is relatively weak; the screening distance is 8 Bohr radii = 4 Å.

```
GET-3DSCH2
LIST
3DSCH2

10   DEF FNV(R)=-EXP(-R/8)/R — Potential, V(r)
20   PRINT "R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?"
30   INPUT R8,R9,R7,L,N,E
40   LET P0=EXP(-R8/N)*R8↑(L+1)        ⎫
50   LET P1=P0*(-R8/N+(L+1)/R8)        ⎬  Initialization at small r
60   LET R=R8                          ⎪
70   PRINT R,P0,P0/R                   ⎭
80   LET R5=(R9-R8)/20
90   LET R6=R+R7/2                     ⎫
100  LET P2=2*(FNV(R6)+L*(L+1)/(2*R6*R6)-E)*(P0+P1*R7/2)  ⎪ Integration of
110  LET P0=P0+(P1+P2*R7/2)*R7         ⎬  the Schrödinger
120  LET P1=P1+P2*R7                   ⎪  equation
130  LET R=R+R7                        ⎭
140  IF R<R5 THEN 170                  ⎫
150  LET R5=R5+(R9-R8)/20              ⎬  Print loop
160  PRINT R,P0,P0/R                   ⎭
170  IF R<R9 THEN 90 — Return for next Δr
180  PRINT
190  GOTO 20
200  END
```

The variables P0, P1, and P2 are the values of P, P', and P'' for each radial distance r in turn. The print-test is not a necessary part of the strategy, but it saves printing out every answer—all several hundred of them for each energy guess.

The ground state is expected to have the orbital angular momentum quantum number, $\ell = 0$. If some other state has lower energy, you'll find out when you search for that state. The unscreened Coulomb potential (the hydrogen atom) has energies (in atomic units) $E = -1/(2n^2)$. So we hunt near $E = -.5$; the difference from $E = -.5$ that you will see in a moment is real and is due to the screening.

You need not use the analytic result for the hydrogen atom to guess your energies; you could look at experimental results instead. From optical experiments on the spectrum of hydrogen, the energy levels can be written as $E = -\text{Ryd}/n^2$, where Ryd = .5. You need not have a good guess for your first energy trial; you'll home in on the eigenvalue sooner or later. It helps to think about your first energy guess because you will home in on the answer more quickly.

SAMPLE EXERCISE

Let's walk through a typical exercise. For the potential $V(r) = -\exp(-r/8)/r$:

1. Plot the $\ell = 0$ (s state) and $\ell = 1$ (p state) effective potentials from $r = 0$ through $r = 5$.

The program is very simple. A printing version might look like this:

```
3DPOT

10   FOR X0=.2 TO 5 STEP .2
20   LET V=-EXP(-X0/8)/X0
30   PRINT X0,V,V+2/(2*X0*X0)
40   NEXT X0
50   END

END
RUN
3DPOT
```

.2	-4.87655	20.1235
.4	-2.37807	3.87193
.6	-1.54624	1.23154
.8	-1.13105	.431453
1	-.882497	.117503
1.2	-.717257	-2.28122E-02
1.4	-.599612	-8.94082E-02
1.6	-.511707	-.121082
1.8	-.44362	-.134978
2	-.3894	-.1394
2.2	-.34526	-.138648
2.4	-.308674	-.135063
2.6	-.277895	-.129966
2.8	-.251674	-.124123
3.	-.229097	-.117985
3.2	-.209475	-.111819
3.4	-.192285	-.10578
3.6	-.177119	-9.99585E-02
3.8	-.163654	-9.44019E-02
4.	-.151633	-8.91327E-02
4.2	-.140847	-8.41572E-02
4.4	-.131125	-7.94721E-02
4.6	-.122327	-7.50682E-02
4.8	-.114336	-.070933
5.	-.107052	-6.70523E-02

```
END
```

Terminal plotting (as discussed in the Appendix) could also be used. The changes in the program and output might look like:

```
5    READ X8,X9,Y8,Y9
6    DATA 0,5,-1,1
7    GOSUB 9000
10   FOR X8=.2 TO 5 STEP .2
20   LET V=-EXP(-X8/5)/X8
30   LET Z8=1
31   LET Y8=V
32   GOSUB 9100
33   LET Z8=2
34   LET Y8=V+2/(2*X8+X8)
35   GOSUB 9100
40   NEXT X8
41   LET Z8=X8=Y8=0
42   GOSUB 9100
45   GOSUB 9200
50   END

APPEND-TTYPLO
RUN
3DPOT
```

```
MAX Y= 1
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y
Y
.Y
Y
Y
Y
Y
Y
Y
Y
Y
Y         2
Y
Y
Y
Y         2
Y
Y8        2
Y          2                               2  2  2   2 2  2
Y           2  2  2  2  2 2  2  2  2  2                  1  1  1   1 1  1  1
Y                                     1  1  1 1
Y
Y                            1  1
Y                        1  1
Y                      1
Y                   1
Y                 1
Y             1
Y
Y           1
Y
Y        1
Y
Y
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y=-1    MIN X= 0                         MAX X= 5
```

2.(a) *Sketch the radial wave function of the lowest $\ell=0$ state. Now find the energy and wave function for this state with the computer.*

We use the second three-dimensional Schrödinger equation program discussed above (the one which initializes P and P' near r=0. The energy of the hydrogen atom for this state is E = -.5. From the RUN you can see that the equivalent screened Coulomb energy is about -.384. So the state has been shifted in energy due to the screening. The wave function is very similar to that of the hydrogen atom at small r but falls off faster than the unscreened wave function at large r.

```
RUN
3DSCH2

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,10,.01,0,1,-.5
  1.00000E-08    1.00000E-08     1.
  .51            .310115         .608069
  1.01           .390447         .386582
  1.51           .392198         .259734
  2.01           .381859         .18998
  2.50001        .391614         .156645
  3.00002        .441881         .147293
  3.50003        .552675         .157906
  4.00004        .752022         .188004
  4.50006        1.08464         .241029
  5.00007        1.62346         .324689
  5.50008        2.48724         .452219
  6.00009        3.86882         .644793
  6.5001         6.08103         .935528
  7.00011        9.6315          1.37591
  7.50012        15.3447         2.04593
  8.00014        24.5615         3.07014
  8.50015        39.4649         4.64285
  9.00016        63.6137         7.06807
  9.50017        102.815         10.8225
  10.0002        166.556         16.6553

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,10,.01,0,1,-.35
  1.00000E-08    1.00000E-08     1.
  .51            .305322         .59867
  1.01           .362477         .358888
  1.51           .319217         .211402
  2.01           .241372         .120086
  2.50001        .159243         6.36968E-02
  3.00002        7.92664E-02     .026422
  3.50003        3.69997E-03     1.05713E-03
  4.00004        -7.17993E-02    -1.79496E-02
  4.50006        -.154643        -3.43646E-02
  5.00007        -.255051        -5.10096E-02
  5.50008        -.386882        -7.03412E-02
  6.00009        -.569407        -9.48997E-02
  6.5001         -.830197        -.127721
  7.00011        -1.2095         -.172784
  7.50012        -1.76683        -.235574
  8.00014        -2.59081        -.323846
  8.50015        -3.81401        -.4487
  9.00016        -5.63528        -.626131
  9.50017        -8.35335        -.879285
  10.0002        -12.4177        -1.24175

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,10,0.01,0,1,-.384
  1.00000E-08    1.00000E-08     1.
  .51            .306405         .680794
  1.01           .36873          .365079
  1.51           .335219         .221999
  2.01           .271278         .134964
  2.50001        .20678          8.27118E-02
  3.00002        .149724         4.99077E-02
  3.50003        .103993         .029712
  4.00004        6.85428E-02     1.71355E-02
  4.50006        4.10359E-02     9.11898E-03
  5.00007        1.88119E-02     3.76233E-03
  5.50008        -8.10361E-04    -1.47336E-04
  6.00009        -2.05754E-02    -3.42918E-03
  6.5001         -4.35395E-02    -6.69827E-03
  7.00011        -7.34854E-02    -1.04977E-02
  7.50012        -.115534        -1.54042E-02
  8.00014        -.177038        -2.21294E-02
  8.50015        -.268917        -3.16367E-02
  9.00016        -.467663        -4.52951E-02
  9.50017        -.618411        -6.50948E-02
  10.0002        -.939641        -9.39624E-02

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?
END
```

2.(b) Sketch the radial wave function for the first excited ℓ=0 state. Now find the energy and wave function for this state with the computer.

We use the same program. The energy for a hydrogen atom in this state is E = -.125. From the RUN you can see that this state is almost lost to the continuum (i.e., E = -.0375 is nearly positive).

```
RUN
3DSCH2

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,10,.01,0,2,-.125
 1.00000E-08     1.00000E-08        1.
  .51             .298207            .58472
 1.01             .322358            .319167
 1.51             .220945            .146321
 2.01             6.97935E-02        3.47232E-02
 2.50001          -8.90025E-02       -3.56809E-02
 3.00002          -.244526           -.081508
 3.50003          -.387851           -.110814
 4.00004          -.519923           -.129979
 4.50005          -.645218           -.14338
 5.00007          -.770076           -.154013
 5.50008          -.90191            -.163981
 6.00009          -1.04896           -.174824
 6.5001           -1.22038           -.187748
 7.00011          -1.42656           -.203792
 7.50012          -1.67963           -.223947
 8.00014          -1.99409           -.249257
 8.50015          -2.38768           -.280899
 9.00016          -2.88243           -.320265
 9.50017          -3.50595           -.36904
10.0002           -4.29308           -.4293

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,20,.01,0,2,-.03
 1.00000E-08     1.00000E-08        1.
 1.01             .306065            .303035
 2.01             1.00067E-02        4.97845E-03
 3.00002          -.320202           -.106733
 4.00004          -.53714            -.134284
 5.00007          -.626289           -.125256
 6.00009          -.619001           -.103165
 7.00011          -.550657           -.078664
 8.00014          -.44896            -.056119
 9.00016          -.332253           -3.69163E-02
10.0002           -.211038           -2.11034E-02
11.0002           -9.00691E-02       -8.18795E-03
12.0002           2.98537E-02        2.48776E-03
13.0002           .15061             1.15852E-02
14.0003           .275959            .019711
15.0003           .411125            2.74078E-02
16.0003           .562671            3.51663E-02
17.0001           .738602            4.34468E-02
18.01             .950962            5.28019E-02
19.0098           1.20758            6.35242E-02
20.0096           1.52516            7.62213E-02

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,20,.01,0,2,-.035
 1.00000E-08     1.00000E-08        1.
 1.01             .306913            .303875
 2.01             1.29796E-02        6.45753E-03
 3.00002          -.316965           -.105654
 4.00004          -.537928           -.13448
 5.00007          -.636199           -.127238
 6.00009          -.64284            -.107138
 7.00011          -.592535           -8.46466E-02
 8.00014          -.512354           -6.40432E-02
 9.00016          -.428293           -4.66984E-02
10.0002           -.326891           -3.26886E-02
11.0002           -.237352           -2.15771E-02
12.0002           -.153334           -1.27776E-02
13.0002           -7.42306E-02       -5.70994E-03
14.0003           2.00354E-03        1.43107E-04
15.0003           7.83904E-02        5.22592E-03
16.0003           .158723            9.92002E-03
17.0001           .247555            1.45619E-02
18.01             .351452            1.95143E-02
19.0098           .47502             2.49881E-02
20.0096           .627367            3.13532E-02

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?
END
```

Plots of these two $\ell=0$ states can be made on the terminal (as discussed in the Appendix). The changes in your program and a RUN are:

```
5 READ X8,X9,Y8,Y9
6 DATA 0,10,-.2,1
7 GOSUB 9000
70 LET X0=R
71 LET Y0=P0/R
72 LET Z0=1
73 GOSUB 9100
160 LET X0=R
161 LET Y0=P0/R
162 GOSUB 9100
175 LET Z0=X0=Y0=0
176 GOSUB 9100
180 GOSUB 9200
APPEND-TTYPLO
RUN
3DSCH2

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,10,.01,0,1,-.384
MAX Y= 1
```

```
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y       1
Y
Y
Y
Y
Y
Y
Y          1
Y
Y
Y           1
Y
Y
Y             1
Y               1
Y                 1   1
Y0                      1   1   1   1   1   1   1
Y                                              1   1   1
Y                                                          1
Y
Y
Y
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
  MIN Y=-.2    MIN X= 0                    MAX X= 10
```

```
R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,10,.01,0,2,-.035
MAX Y= 1
```

```
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y        1
Y
Y
Y
Y
Y
Y          1
Y
Y
Y            1
Y
Y0             1
Y
Y                                                    1   1   1
Y                 1                          1   1   1
Y                    1   1   1   1   1   1
Y
Y
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
  MIN Y=-.2    MIN X= 0                    MAX X= 10
R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?
END
```

2.(c) Sketch the radial wave function for the lowest energy ℓ=1 state. Now find the energy wave function for this state with the computer.

We use the same program. The hydrogen atom energy for this state is E = -.125. The lowest p state and the second lowest s state are degenerate in hydrogen. This state is again nearly lost to the continuum for this screened Coulomb case. If the state were lost to the continuum, a RUN for E=0 would not produce enough curvature (the kinetic energy term in the Schrödinger equation) to bring the tail to zero. This state starts out from R(0)=0 and has one (positive) lobe before the tail goes smoothly to zero. The RUN shows that E is about -.0325 atomic units.

```
RUN
3DSCH2

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?1E-8,20,.01,1,2,0
  1.00000E-08     1.00000E-16     1.00000E-08
  1.01           3.04730E-06     3.01713E-06
  2.01           7.26512E-06     3.61449E-06
  3.00002        9.63628E-06     3.21274E-06
  4.00004        9.83324E-06     2.45828E-06
  5.00007        8.28376E-06     1.65672E-06
  6.00009        5.61482E-06     9.35655E-07
  7.00011        2.35942E-06     3.37054E-07
  8.00014       -1.09131E-06    -1.36411E-07
  9.00016       -4.41446E-06    -4.98265E-07
 10.0002        -7.67990E-06    -7.67076E-07
 11.0002        -1.05752E-05    -9.61363E-07
 12.0002        -1.31786E-05    -1.09753E-06
 13.0002        -1.54605E-05    -1.18925E-06
 14.0003        -1.74658E-05    -1.24753E-06
 15.0003        -1.92160E-05    -1.28104E-06
 16.0003        -2.07441E-05    -1.29645E-06
 17.0001        -2.28832E-05    -1.29900E-06
 18.01          -2.32757E-05    -1.29235E-06
 19.0098        -2.43268E-05    -1.27970E-06
 20.0016        -2.52745E-05    -1.26312E-06

R(START),R(END),DELTA-R,ORBITAL #(L),RADIAL #(N),ENERGY?
?
END
```

Since these last two states have different energies, the degeneracy of the unscreened Coulomb potential is broken by even this fairly weak screening.

3. Calculate the difference in energy between the two ℓ=0 states in atomic units, eV, Hertz, and Å.

(1 eV = 1.602 x 10^{-12} ergs; h = 6.624 x 10^{-27} erg-sec; c = 2.998 x 10^{10} cm/sec)

E = -.038 + .384 = .346 atomic units = 9.41 eV = 1.51 x 10^{-11} ergs.

frequency = 2.28 x 10^{15} Hertz; lambda = 1317 Å.

Note that the wavelength for emission from this transition compares well with the Lyman alpha line (1216 Å). The difference between the second ℓ=0 state and the lowest ℓ=1 state is .005 atomic units=.136 eV. The spectral line for this transition has lambda=91110 Å (in the infrared).

4. Plot the probability distribution of the full wave function ψ(r,θ,φ) = R(r)Y(θ,φ) in the φ=0- φ=180 plane for the ground state (the lowest-lying ℓ=0 state).

Terminal plotting can be used. The following program stores the radial and angular parts of the wave function and then finds the current combination for each point plotted.

```
3DR-T

10   DEF FNV(R)=-EXP(-R/8)/R—  Potential, V(r)
20   DIM T[401],R[402]
30   PRINT "R(START),R(END),ORBITAL #(L),ENERGY?"
40   INPUT R8,R9,L,E                    ⎫
50   LET R7=(R9-R8)/400                 ⎬  Initialization
60   LET T7=3.14159/400                 ⎭
70   LET R0=T0=0
80   FOR I=1 TO 401                     ⎫
90   LET T=-3.14159/2+(I-1)*T7          ⎪
100  LET T[I]=1                         ⎬  Calculation of
110  IF L=0 THEN 130                    ⎪  Θ(θ);
120  LET T[I]=(COS(T))↑2                ⎬  stored in T( )
130  IF T[I]<T0 THEN 150                ⎪
140  LET T0=T[I]                        ⎪
150  NEXT I                             ⎭
160  LET R=R8                           ⎫
170  LET P0=R↑(L+1)                     ⎬  Initialization of R(r)
180  LET P1=(L+1)*R↑L                   ⎪
190  LET I=1                            ⎪
200  LET R[I]=P0*P0/(R*R)               ⎭
210  LET R6=R+R7/2                      ⎫  Integration
220  LET P2=2*(FNV(R6)+L*(L+1)/(2*R6*R6)-E)*(P0+P1*R7/2)  ⎪ of the
230  LET P0=P0+(P1+P2*R7/2)*R7          ⎬  Schrödinger
240  LET P1=P1+P2*R7                    ⎪  equation
250  LET R=R+R7                         ⎫
260  LET I=I+1                          ⎬  Store R²(r)/r² in R( )
270  LET R[I]=P0*P0/(R*R)               ⎭
280  IF R[I]<R0 THEN 300                ⎫
290  LET R0=R[I]                        ⎬  Find [R²(r)/r²]max
300  IF R<R9+R7/2 THEN 210              ⎭
310  PRINT "MAX. R=";R0;"    MAX. T=";T0
320  PRINT "LEFT X, RIGHT X, BOTTOM Y, TOP Y, MAX. FOR Z?"  ⎫ Initialize
330  INPUT X8,X9,Y8,Y9,Z9                                    ⎬ plot
340  GOSUB 9000
350  FOR X0=X8 TO X9 STEP (X9-X8)/14—  Step across x
360  FOR Y0=Y8 TO Y9 STEP (Y9-Y8)/10—  Step across y
370  IF ABS(X0)+ABS(Y0)=0 THEN 490     ⎫
380  LET R=SQR(X0*X0+Y0*Y0)            ⎪
390  IF R>(R9-R8) THEN 490             ⎪
400  LET I0=1+INT(R/R7+.5)             ⎬  Find right elements
410  IF X0 <> 0 THEN 440               ⎪  of R( ) and T( )
420  LET I1=1                          ⎪
430  GOTO 450                          ⎭
440  LET I1=201+INT(ATN(Y0/X0)/T7+.5)  ⎭
450  LET Z0=INT(9*R[I0]*T[I1]/Z9+.5)—  Find right character for |ψ|²
460  IF Z0*(Z0-8) <= 0 THEN 480        ⎫ Force all too-big |ψ|² to be 9
470  LET Z0=9                          ⎭
480  GOSUB 9100—Store point in plot
490  NEXT Y0
500  NEXT X0
510  GOSUB 9200—Print out the plot
520  PRINT
530  GOTO 320—Return for new plot
540  STOP

END
```

```
RUN
3DR-T

R(START),R(END),ORBITAL #(L),ENERGY?
?1E-8,5,0,-.384
MAX. R= .975235    MAX. T= 1
LEFT X, RIGHT X, BOTTOM Y, TOP Y, MAX. FOR Z0?
?-1.4,1.4,-1,1,1
MAX Y= 1
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y0    0    1    1    1    1    1    1    1    1    1    1    1    0
Y
Y
Y0    1    1    1    1    1    2    2    2    1    1    1    1    1
Y
Y
Y0    1    1    1    2    2    3    3    3    2    2    1    1    1
Y
Y
Y0    1    1    1    2    3    4    4    4    3    2    1    1    1
Y
Y
Y1    1    1    2    3    4    5    6    5    4    3    2    1    1
Y
Y
Y1    1    1    2    3    4    6    9    6    4    3    2    1    1
Y
Y
Y1    1    1    2    3    4    5    6    5    4    3    2    1    1
Y
Y
Y0    1    1    1    2    3    4    4    4    3    2    1    1    1
Y
Y
Y0    1    1    1    2    2    3    3    3    2    2    1    1    1
Y
Y
Y0    1    1    1    1    1    2    2    2    1    1    1    1    1
Y
Y
Y0    0    1    1    1    1    1    1    1    1    1    1    1    0
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y=-1   MIN X=-1.4                        MAX X= 1.4

LEFT X, RIGHT X, BOTTOM Y, TOP Y, MAX. FOR Z0?
?
END
```

EXERCISES — Use computer when appropriate.

I. For the screened Coulomb potential $V(r) = -\exp(-r/10)/r$:

   1. Plot the effective potential for $\ell = 0$ and $\ell = 1$.

   2.(a) Find the radial wave function and the energy for the lowest energy $\ell = 0$ state.

   2.(b) Find the radial wave function and the energy for the first excited $\ell = 0$ state.

   2.(c) Find the radial wave function and the energy for the lowest energy $\ell = 1$ state.

   3. Calculate the difference in energy between the two $\ell = 0$ states in atomic units, eV, Hertz, and Å.

   4. Plot the probability distribution of the full wave function $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ in the $\phi = 0 - \phi = 180°$ plane for the lowest lying p state.

   Hint: Use the program which initializes P(r) near the origin.

II. For the screened Coulomb potential $V(r) = -\exp(-r/5)/r$:

   1. Plot the effective potential for $\ell = 0$ and $\ell = 1$.

   2.(a) Find the radial wave function and the energy of the lowest $\ell = 0$ state.

  2.(b) Find the radial wave function and the energy for the first excited $\ell = 0$ state.

  2.(c) Find the radial wave function and the energy for the lowest energy $\ell = 1$ state.

  3. Calculate the difference in energy between the two $\ell = 0$ states in atomic units, eV, Hertz, and Å.

  4. Plot the probability distribution of the full wave function $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ in the $\phi = 0 - \phi = 180°$ plane for the lowest-lying p state.

  Hint: Use the program which initializes P(r) near the origin.

III. For the Lennard-Jones 6–12 potential, $V(r) = 400\,(1/r^{12} - 1/r^{6})$:

  1. Plot the effective potential for $\ell = 0$ and $\ell = 1$.

  2.(a) Find the radial wave function and the energy of the lowest $\ell = 0$ state.

  2.(b) Find the radial wave function and the energy for the first excited $\ell = 0$ state.

  2.(c) Find the radial wave function and the energy for the lowest energy $\ell = 1$ state.

  3. Calculate the difference in energy between the two $\ell = 0$ states in atomic units, eV, Hertz, and Å.

  4. Plot the probability distribution of the full wave function $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ in the $\phi = 0 - \phi = 180°$ plane for the lowest-lying p state.

  Hint: Use the program which initializes P(r) at large r.

IV. For the screened Coulomb potential $V(r) = -\exp(-r)/r$:

  1. Plot the effective potential for $\ell = 0$ and $\ell = 1$.

  2.(a) Find the radial wave function and the energy of the lowest $\ell = 0$ state.

  2.(b) Find the radial wave function and the energy for the first excited $\ell = 0$ state.

  2.(c) Find the radial wave function and the energy for the lowest energy $\ell = 1$ state.

  3. Calculate the difference in energy between the two $\ell = 0$ states in atomic units, eV, Hertz, and Å.

  4. Plot the probability distribution of the full wave function $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ in the $\phi = 0 - \phi = 180°$ plane for the lowest-lying p state.

  Hint: Use the program which initializes P(r) near the origin.

*V. For the potential family, $V(r) = 400 * (r^{-12} - r^{-m})$:

  1. Find the ground state energy and wave function for m=3, 4, 6, and 10.

  2. Plot the energy of the ground state as a function of m.

  3. Find the small r and large r behaviors of each wave function.

4. *Can you extrapolate your results to all m?*

*VI. For the potential family, $V(r) = -\exp(-r/r_0)/r$:

1. *Find the ground state energies and wave functions for r=1, 2, 4, 8, and 12.*

2. *Plot the energies versus the screening parameter, r_0.*

3. *Find the small r and large r behavior of each wave function.*

4. *Can you generalize your results to all screening parameters, r_0?*

**VII. For the potential family, $V(r) = -1/r^m$:

1. *Find the ground state energies and wave functions for m=1, 3, 6, and 10.*

2. *Plot the energies of the ground states as a function of m.*

3. *Find the small r and large r behavior of each wave function.*

4. *Can you extrapolate your results to the behavior of these ground states for all m?*

CHAPTER THREE: THE ONE-DIMENSIONAL, TIME-DEPENDNT, SCHRÖDINGER EQUATION FOR TIME-INDEPENDENT POTENTIALS

INTRODUCTION

The time-dependent Schrödinger equation in one dimension is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x,t)\,\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{21}$$

If the potential, $V(x,t)$, is independent of time, $V=V(x)$, then the equation separates by setting $\psi(x,t) = P(x)T(t)$. The equation for $P(x)$ is the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2P}{dx^2} + V(x)P = EP \tag{22}$$

The equation for $T(t)$ is

$$\frac{dT}{dt} = -i\frac{E}{\hbar}T \tag{23}$$

E is the separation constant and, as you can see from its position in Equation (22), plays the role of the energy.

The equation for $T(t)$ (Equation (23)) solves immediately to

$$T(t) = A\,e^{-i\frac{E}{\hbar}t} \tag{24}$$

which in Hartree atomic units (see the Preface) is

$$T(t) = A\,e^{-iEt} \tag{25}$$

The constant A is just a normalization constant.

The spatial equation (Equation (1)) can be solved analytically (for a few problems) or numerically as discussed in Chapter One. This chapter emphasizes the effects of the time part of the full wave function $\psi(x,t) = P(x)\exp(-iEt)$.

STATES OF THE INFINITE SQUARE WELL

The infinite square well,

$$V(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 < x < L \\ \infty & x > L \end{cases} \tag{26}$$

can be solved analytically. The result is standing waves whose spatial wave functions are

$$P_n(x) = B_n \sin(n\pi x/L) \qquad n = 1, 2, \cdots \tag{27}$$

B_n being a normalization constant. The full wave function for these discrete states are then

$$\psi_n(x,t) = C_n \sin(n\pi x/L)\,e^{-iE_nt} \tag{28}$$

The energies of the states are

$$E_n = \frac{1}{2}\left(\frac{\pi}{L}\right)^2 n^2 \qquad n = 1, 2, \cdots \qquad (29)$$

THE BEHAVIOR OF SETS OF DISCRETE STATES

Consider setting up a particular shape for the electron's distribution at time = 0. For definiteness, let's set up (an approximation to) a square wave with ½ wavelength in the well. By the ideas of Fourier Series, we know that we want to add up a number of these discrete states (in particular, those with n = 1, 3, 5, 7, ...) with varying amounts for each n. If we write

$$\text{square wave} = \Sigma A_n P_n (x)$$

then the A_n's are proportional to $1/n$ in order to produce a square wave.

After setting up such a shape at t=0, you then let time start passing. Each mode of the well will oscillate in time with its own angular frequency $\omega_n = E_n/\hbar$ or $\omega_n = E_n$ in atomic units. The energy depends on the wavelength squared or the wave vector of the state squared. The higher energy modes run ahead of the lower energy modes, and the shape distorts away from a square wave.

This result is unlike the result of a square standing wave on a stretched string. On a stretched string, the speeds of the various waves are independent of the wavelengths (or wave vectors $k_n = n\pi/L$ for the discrete states). The speed, v, of waves on a string depends only on the parameters of the string (tension, etc.).

In the case of these electron waves, the speed of the wave, $v = \omega/k = E/\hbar k = \hbar k/2m$ or $v = k/2$ in atomic units. The speed depends on the wave vector (that is, the wavelength). This is an example of what is called a dispersive medium. The vacuum (where $V(x) = 0$ everywhere) is a dispersive medium for electron waves.

Let's watch the time development of our electron square wave in the infinite square well. A program (and its RUN) to perform the sums and products necessary might be:

```
VELSET
10    DIM A(15,21),E(15),C(15),S(15)
20    LET PI=3.14159        Length of well
30    LET L=1
40    FOR I=1 TO 15         Step through 15 states
50    LET N=2*(I-1)+1
60    LET K0=N*PI/L
70    LET E(I)=K0*K0/2       Energy of each state
80    FOR J=1 TO 21          Step across x
90    LET X0=(J-1)*L/20
100   LET A(I,J)=SIN(K0*X0)/N   Spatial wave function
110   NEXT J
120   NEXT I
130   PRINT "TIME?"
140   INPUT T0
150   FOR I=1 TO 15
160   LET C(I)=COS(E(I)*T0)     }  Store exp(-iEt)
170   LET S(I)=SIN(-E(I)*T0)
180   NEXT I
190   FOR J=1 TO 21          Step across x
200   LET X0=(J-1)*L/20
210   LET A1=A2=0            Step through 15 states
220   FOR I=1 TO 15
230   LET A1=A1+A(I,J)*C(I)    Real part of ψ(x,t)
240   LET A2=A2+A(I,J)*S(I)    Imaginary part
250   NEXT I
260   PRINT X0,A1*A1+A2*A2
270   NEXT J
280   PRINT
290   GOTO 130     Return for new time
300   END
```

Store energies and spatial wave function for each state

```
RUN
WEL SET

TIME?
70
0            0
.05          .646566
.1           .702685
.15          .613192
.2           .573336
.25          .618071
.3           .649561
.35          .616355
.4           .589667
.45          .616991
.5           .643279
.55          .616989
.6           .589667
.65          .616355
.7           .649561
.75          .618072
.8           .573335
.85          .61319
.9           .702685
.95          .646569
1            1.06422E-12

TIME?
?1
0            0
.05          .109818
.1           6.21948E-02
.15          .295673
.2           .551871
.25          .690341
.3           .434205
.35          .689529
.4           .740919
.45          1.58383
.5           1.88855
.55          1.58383
.6           .74092
.65          .689528
.7           .434204
.75          .69034
.8           .55187
.85          .295672
.9           6.21952E-02
.95          .109818
1            1.74060E-13

TIME?
?2
0            0
.05          .124334
.1           4.38285E-02
.15          9.81896E-02
.2           .344567
.25          .148464
.3           .651564
.35          .942334
.4           1.23172
.45          1.35741
.5           2.25539
.55          1.35741
.6           1.23172
.65          .942334
.7           .651561
.75          .148464
.8           .344566
.85          9.81895E-02
.9           4.38286E-02
.95          .124333
1            5.16420E-13

TIME?
?
END
```

Terminal plotting (as discussed in the Appendix) can also be used. The changes you might make in the program and a RUN follow:

```
5 READ X8,X9,Y8,Y9
6 DATA 0,1,0,2.5
7 GOSUB 9000
260 LET Y0=A1*A1+A2*A2
270 LET Z0=1
270 NEXT J
262 LET Z0=1
264 GOSUB 9100
280 GOSUB 9200
APPEND-TTYPLO
RUN
WELSET

TIME?
?0
MAX Y= 2.5
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y         I  I          I             I           I        I  I
Y          I  I  I       I  I  I     I  I  I     I  I  I
Y
Y
Y
Y
Y
Y1                                                    I
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y= 0   MIN X= 0                    MAX X= 1


TIME?
?1
MAX Y= 2.5
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y
Y
Y
Y
Y
Y
Y
Y
Y                      I
Y
Y
Y               I       I
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y               I       I
Y            I     I           I     I
Y          I               I
Y       I              I
Y              I             I
Y          I                   I
Y1  I  I                        I  I
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y= 0   MIN X= 0                    MAX X= 1
```

```
TIME?
72
MAX Y= 2.5
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y
Y
Y
Y                                   I
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y                          I      I
Y                       I            I
Y
Y
Y
Y                   I                     I
Y
Y                I                           I
Y
Y
Y
Y            I                                  I
Y
Y         I           I                            I
Y I    I   I                                        I  I   I
Y I                                                          I
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y= 0    MIN X= 0                   MAX X= 1
TIME?
?
END
```

This same sort of procedure can be carried out for the discrete states of any one-dimensional potential. If an analytic solution to the problem exists, it is usually more efficient to use that. If an analytic solution does not exist, you can solve numerically for the spatial wave function, P(x), as discussed in Chapter One. The same sort of procedure can be carried out for states in a continuum (for example, the states of a finite square well whose energies lie above the top of the well). Before we discuss the behavior of sets of continuum states as time passes, we need to discuss the spatial wave function solutions for one-dimensional continuum states.

ONE-DIMENSIONAL CONTINUUM STATES

Suppose we have some potential well such that, for $|x| > x_0$, the potential, $V(x)$, is essentially zero. Then, for $|x| > x_0$, the Schrödinger equation for the spatial wave function, $P(x)$, becomes

$$P''(x) = -2EP(x) \tag{30}$$

The solution for $P(x)$ is $P(x) = \exp(+ikx)$, $\exp(-ikx)$ or, equivalently, $P(x) = \cos(kx)$, $\sin(kx)$. Neither solution must be discarded because of boundary conditions; both solutions are well-behaved everywhere; there is no classically forbidden region for large x which forces one or the other solution to be unphysical. There are two solutions to the equation for every energy, E. Furthermore, since there are no boundary conditions which limit the acceptable energies, every energy, E, is allowed. Hence the states form a continuum of pairs of states.

If the potential, $V(x)$, is symmetric, the theorem discussed in Chapter One (and the Appendix) tells us we can choose the states to be wholly even in x or wholly odd in x if we wish. Since any linear combination of solutions to the Schrödinger equation is itself a solution, we could choose any arbitrary phase and make $\sin(kx+\phi)$ one of our two solutions; the other solution (by orthogonality) would then be $\cos(kx+\phi)$.

The simplest potential of the sort we've just been discussing is $V(x) = 0$ everywhere (the free particle). The even and odd wave functions for energy, E, in this potential are $\cos(kx)$ and $\sin(kx)$ where $k = \sqrt{2E}$ in atomic units. The full solutions, $\psi(x,t)$, for the states of energy, E, are then

$$\psi(x,t) = \cos(kx)e^{-ik^2 t/2} \text{ and } \sin(kx)e^{-ik^2 t/2} \tag{31}$$

We will now put together sets of these states to make pulses, or wave packets.

FREE WAVE PACKETS

Since for the continuum we have a large range of closely-spaced allowed energies and wave vectors, we can build up a shaped pulse. Such a pulse is usually known as a wave packet. To make a Gaussian-shaped wave packet, $\exp(-(x/x_0)^2)$, for example, you use a range of wave vectors, k (around k = some central k_0), each with its own amplitude, A(k), where $A(k) \propto x_0 \exp(-(k-k_0)^2 x_0^2/2)$. (This is just a formula you can find in books on Fourier transforms.)

You can build up almost any shaped free packet you wish. For a square wave packet with width x_0, $A(k) = x_0 \sin((k-k_0)x_0/2)/((k-k_0)x_0/2)$. For a triangular wave packet with basic width $2x_0$, $A(k) = x_0 \sin^2((k-k_0)x_0/2)/((k-k_0)x_0/2)^2$. The central wave vector, k_0, determines the speed of the packet. The group velocity is $v = dE/dK = hk_0/m$ or k_0 in atomic units.

The next section discusses what happens when you set up such a wave packet at time equals zero and then let go. Remember that the wave packet is traveling through a dispersive medium; the packet shape will distort and deform as the higher energy states in the packet shift out ahead of the lower states.

THE PROPAGATION OF FREE WAVE PACKETS

A program can easily calculate and add up the amplitudes of the various components of a packet. Because of limitations on how many amplitudes can be stored and how long it may take a program to RUN, an approximation to the continuous distribution of amplitudes, A(k), must be made. Using twenty k's, for example, across the Gaussian A(k) produces a reasonably good Gaussian wave packet in space.

We set up a packet, centered at the origin, at time = 0; we then let time pass and calculate each component's time factor, $\exp(-iEt)$. This part of the full wave function shifts the relative phases of the various components of the wave packet (since each component has its own energy, E). At some later time, you add the phase-shifted components back up. The packet has moved and distorted. Notice that the time parts of the wave functions do nothing to the amplitudes of the states because $|\exp(-iEt)| = 1$.

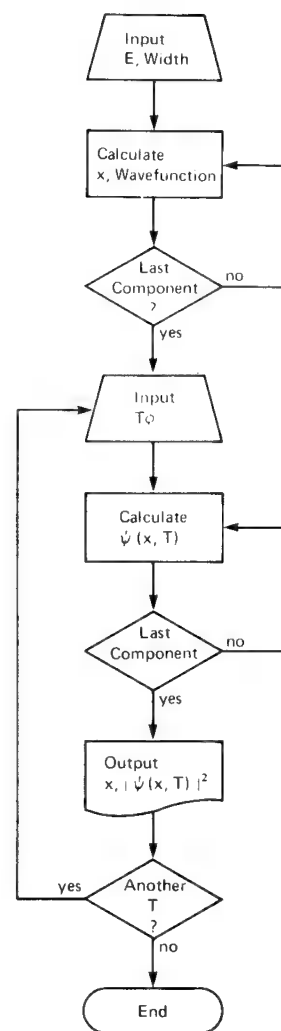Figure 3 shows a block diagram of this strategy. One implementation of this strategy is the following program:

Figure 3.   Flow Chart of Computer Approach to Wavepacket Strategy

TIME-DEPENDENT SCHRÖDINGER EQUATION □ 41

FREPAC

```
10   DIM P(21,26),Q(21,26),E(21),C(21),S(21)
20   PRINT "CENTRAL ENERGY, HALF-WIDTH OF PACKET?"
30   INPUT E8,X6
40   LET K8=SQR(2*E8)←——— Central wave vector
50   LET K9=3/(10*X6)←——— Δk
60   FOR I=1 TO 21←——————Step through states
70   LET K8=K8+(I-11)*K9
80   LET E(I)=K8*K8/2←——— Energy of each state
90   LET K1=K8-K8
100  LET A=.399569*X6*EXP(-X6*X6*K1*K1/2)—Amplitude
110  FOR J=1 TO 26←————— Step across x      of each state
120  LET X8=-2.5+(J-1)*.5
130  LET P(I,J)=A*COS(K8*X8)←—Real part of spatial
140  LET Q(I,J)=A*SIN(K8*X8)   wave function
150  NEXT J                           Imaginary part
160  NEXT I
170  PRINT "TIME THE PACKET HAS PROPAGATED?"
180  INPUT T8
190  FOR I=1 TO 21
200  LET C(I)=COS(E(I)*T8)
210  LET S(I)=SIN(-E(I)*T8)
220  NEXT I
230  FOR J=1 TO 26←————— Step across x
240  LET X8=-2.5+(J-1)*.5
250  LET P1=P2=0
260  FOR I=1 TO 21←————— Step through states
270  LET P1=P1+K9*(P(I,J)*C(I)-Q(I,J)*S(I))←—Real part of ψ(x,t)
280  LET P2=P2+K9*(Q(I,J)*C(I)+P(I,J)*S(I))←—Imaginary part
290  NEXT I
300  PRINT X8,P1*P1+P2*P2
310  NEXT J
320  PRINT
330  GOTO 170←—Return for new propagation time
340  END
```

Store energies and wave functions for several states

Store exp(-iEt)

```
GET-FREPAC
RUN
FREPAC

CENTRAL ENERGY, HALF-WIDTH OF PACKET?
?2,1
TIME THE PACKET HAS PROPAGATED?
?0
-2.5          2.01288E-03
-2            1.80537E-02
-1.5          .105321
-1            .370809
-.5           .781667
 0            1.
 .5           .781667
 1            .370809
 1.5          .105321
 2            1.80537E-02
 2.5          2.01288E-03
 3            1.44026E-04
 3.5          1.56646E-06
 4            7.61904E-08
 4.5          9.50167E-07
 5            1.75886E-07
 5.5          8.03676E-07
 6            7.47309E-08
 6.5          7.27233E-07
 7            2.83461E-08
 7.5          6.63554E-07
 8            7.77053E-09
 8.5          6.15697E-07
 9            4.21349E-10
 9.5          5.85946E-07
 10           1.53330E-09

TIME THE PACKET HAS PROPAGATED?
?1
-2.5          2.36933E-05
-2            2.61658E-04
-1.5          1.59560E-03
-1            7.97562E-03
-.5           3.12858E-02
 0            9.52993E-02
 .5           .22992
 1            .431434
 1.5          .626177
 2            .708069
 2.5          .626177
 3            .431434
 3.5          .22992
 4            9.52989E-02
 4.5          3.12857E-02
 5            7.97564E-03
 5.5          1.59562E-03
 6            2.61660E-04
 6.5          2.36911E-05
 7            2.82795E-06
 7.5          3.00551E-07
 8            1.98935E-07
 8.5          8.83865E-07
 9            1.12792E-07
 9.5          8.47568E-07
 10           4.00021E-06

TIME THE PACKET HAS PROPAGATED?
?3
-2.5          2.46894E-04
-2            4.87908E-04
-1.5          1.11567E-03
-1            2.31684E-03
-.5           4.54715E-03
 0            .008767
 .5           1.53854E-02
 1            .026273
 1.5          4.20155E-02
 2            6.37406E-02
 2.5          9.31304E-02
 3            .128852
 3.5          .169734
 4            .213225
 4.5          .253389
 5            .286229
 5.5          .309357
 6            .318079
 6.5          .309357
 7            .286228
 7.5          .253389
 8            .213224
 8.5          .169734
 9            .128852
 9.5          9.31303E-02
 10           6.37405E-02

TIME THE PACKET HAS PROPAGATED?
?
END
```
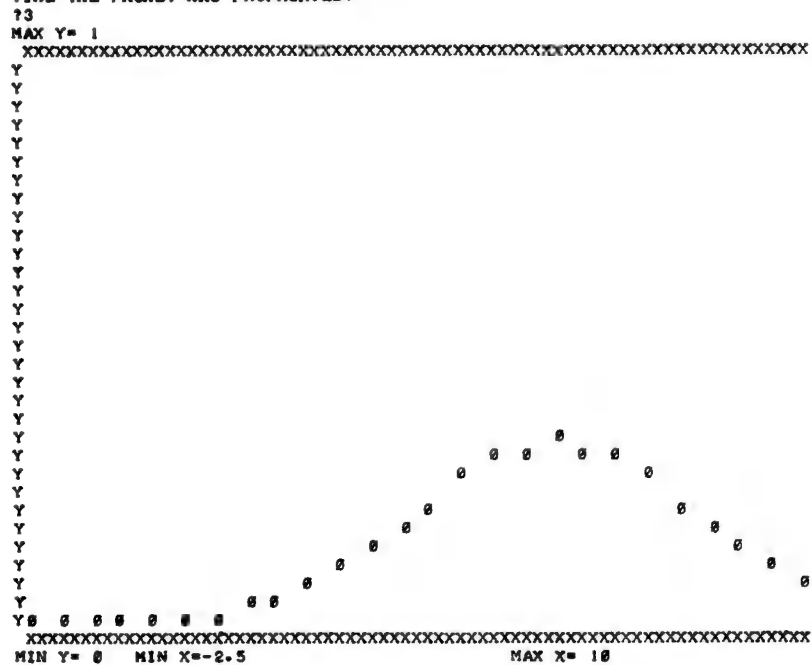
To use terminal plotting you might make the following changes:

```
5 READ X8,X9,Y8,Y9,Z8
6 DATA -2.5,10,8,1,8
7 GOSUB 9000
300 LET Y8=P1+P1+P2+P2
302 GOSUB 9100
320 GOSUB 9200
APPEND-TTYPLO
RUN
FREPAC

CENTRAL ENERGY, HALF-WIDTH OF PACKET?
?2,1
TIME THE PACKET HAS PROPAGATED?
?0
MAX Y= 1
```



```
MIN Y= 0    MIN X=-2.5                   MAX X= 10
TIME THE PACKET HAS PROPAGATED?
?1
MAX Y= 1
```



```
MIN Y= 0    MIN X=-2.5                   MAX X= 10
```

```
TIME THE PACKET HAS PROPAGATED?
?3
MAX Y= 1
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y                                     0 0
Y                               0 0  0  0 0
Y                            0                  0
Y                         0                        0
Y                       0                            0
Y                     0                                0
Y                   0                                    0
Y                 0                                        0
Y               0                                            0
Y            0 0                                               0
Y0  0  0 0  0  0  0  0
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y= 0   MIN X=-2.5                      MAX X= 10
```

THE PROPAGATION OF A PACKET
OVER A POTENTIAL WELL

You can also use this strategy to propagate wave packets by potential wells.
For a general (symmetric) potential well, you could calculate the spatial wave
functions numerically as discussed in Chapter One. The strategy of the calcu-
lation is the same as that for free packets. The only difference is the calculation
of the spatial wave function.

We will form our packet at x = 0 to the left of the well; we will then start the
packet towards the well. In the end, part of the packet will get past the well;
part will be reflected. Some of you may have seen the films of the quantum
mechanical scattering of packets off the finite square well. The smoother the
potential, the easier it is for the packet to get past. Smooth edges on the
potential also diminish the rapid oscillations (the interference effects) at the
edges of the well.

A program to propagate wave packets by potential wells might look like the following:

```
GET-VPAC
LIST
VPAC

10   DIM P[21,26],Q[21,26],E[21],C[21],S[21]
20   DEF FNV(X)=-100*EXP(-(X-6)*(X-6))          ──Potential, V(x)
30   PRINT "CENTRAL ENERGY, HALF-WIDTH OF PACKET?"
40   INPUT E8,X6
50   LET K8=SQR(2*E8)
60   LET K9=3/(10*X6)
70   LET X1=.1
80   FOR I=1 TO 21◄──Step through states
90   LET K0=K8+(I-11)*K9
100  LET E[I]=K0*K0/2 ◄──Energy of each state
110  LET K7=K0-K8
120  LET A=.399569*X6*EXP(-X6*X6*K7*K7/2)◄── ──Amplitude of
130  LET Q[I,1]=Q0=P1=0                           each state
140  LET P[I,1]=P0=A
150  LET Q1=K0*A                           Initialize calculation
160  LET X0=X5=0                           of radial wave function
170  LET N=1
180  LET K1=P1
190  LET M1=Q1
200  LET L0=2*(FNV(X0)-E[I])
210  LET L1=L0*P0
220  LET N1=L0*Q0
230  LET K2=P1+L1*X1/2
240  LET M2=Q1+N1*X1/2
250  LET L0=2*(FNV(X0+X1/2)-E[I])          Fourth Order
260  LET L2=L0*(P0+K1*X1/2)                Runge-Kutta
270  LET N2=L0*(Q0+M1*X1/2)                calculation of
280  LET K3=P1+L2*X1/2                     real and imaginary
290  LET M3=Q1+N2*X1/2                     parts of radial
300  LET L3=L0*(P0+K2*X1/2)                wave function
310  LET N3=L0*(Q0+M2*X1/2)
320  LET K4=P1+L3*X1
330  LET M4=Q1+N3*X1
340  LET L0=2*(FNV(X0+X1)-E[I])
350  LET L4=L0*(P0+K3*X1)
360  LET N4=L0*(Q0+M3*X1)
370  LET P0=P0+X1*(K1+2*K2+2*K3+K4)/6
380  LET P1=P1+X1*(L1+2*L2+2*L3+L4)/6
390  LET Q0=Q0+X1*(M1+2*M2+2*M3+M4)/6
400  LET Q1=Q1+X1*(N1+2*N2+2*N3+N4)/6
410  LET X0=X0+X1
420  LET X5=X5+X1
430  IF ABS(X5-.5)>X1/2 THEN 480           Store real and
440  LET X5=0                              imaginary parts
450  LET N=N+1                             of spatial wave functions
460  LET P[I,N]=P0
470  LET Q[I,N]=Q0
480  IF X0<12.6 THEN 180◄──Return for next △x
490  NEXT I
500  PRINT "TIME THE PACKET HAS PROPAGATED?"
510  INPUT T0
520  FOR I=1 TO 21
530  LET C[I]=COS(E[I]*T0)                 Store exp(-iEt)
540  LET S[I]=SIN(-E[I]*T0)
550  NEXT I
560  FOR J=1 TO 26◄──Step across x
570  LET X0=(J-1)*.5
580  LET P1=P2=0
590  FOR I=1 TO 21◄──Step through states
600  LET P1=P1+K9*(P[I,J]*C[I]-Q[I,J]*S[I])◄──Real ψ(x,t)
610  LET P2=P2+K9*(Q[I,J]*C[I]+P[I,J]*S[I])◄──Imaginary ψ(x,t)
620  NEXT I
630  PRINT X0,P1*P1+P2*P2
640  NEXT J
650  PRINT
660  GOTO 500◄──Return for now propagation time
670  END
```

```
RUN
VPAC

CENTRAL ENERGY, HALF-WIDTH OF PACKET?
?18,1
TIME THE PACKET HAS PROPAGATED?
?8
0               1.
.5              .781693
1               .371724
1.5             .186117
2               .618311
2.5             2.05115E-03
3               1.47756E-04
3.5             1.79255E-06
4               6.89511E-08
4.5             2.15275E-07
5               3.11387E-07
5.5             1.37568E-07
6               2.79572E-08
6.5             2.55129E-09
7               1.56037E-08
7.5             7.41130E-08
8               6.41582E-08
8.5             2.06862E-07
9               1.98623E-07
9.5             1.21517E-07
10              1.01854E-06
10.5            2.39367E-06
11              1.71395E-06
11.5            3.14085E-06
12              2.97387E-06
12.5            1.72569E-06


TIME THE PACKET HAS PROPAGATED?
?1.5
0               2.67713E-06
.5              4.86381E-06
1               3.57881E-05
1.5             1.41887E-04
2               6.59903E-04
2.5             2.39183E-03
3               8.84472E-03
3.5             2.29557E-02
4               5.03398E-02
4.5             6.18695E-02
5               5.44877E-02
5.5             4.34922E-02
6               3.81167E-02
6.5             2.62809E-02
7               3.84742E-02
7.5             7.78667E-02
8               .141367
8.5             .17333
9               .160835
9.5             .121498
10              7.68528E-02
10.5            3.85898E-02
11              1.65678E-02
11.5            5.88771E-03
12              1.71766E-03
12.5            4.59441E-04
```

Using terminal plotting you get:

```
CENTRAL ENERGY, HALF-WIDTH OF PACKET?
?10,1
TIME THE PACKET HAS PROPAGATED?
?0
MAX Y= 1
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y!
Y
Y
Y
Y
Y
Y
Y
Y     1
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y     1
Y
Y
Y
Y
Y
Y
Y
Y     1
Y
Y         1
Y      1
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y= 0   MIN X= 0              MAX X= 12.5


TIME THE PACKET HAS PROPAGATED?
?1.5
MAX Y= 1
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y                             1 1
Y                           1     1
Y
Y             1 1 1       1
Y           1     1 1 1 1       1
Y! 1 1 1 1 1 1                         1  1  1  1
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y= 0   MIN X= 0              MAX X= 12.5
TIME THE PACKET HAS PROPAGATED?
?
END
```

The program uses a fourth-order Runge-Kutta method of integration to find the spatial wave function. Adding up wave functions to make packets demands that not only the amplitudes of the wave functions but also the phases must be very accurate. You must be careful to use a small enough space step.

Because of the limitations of some computers, only 21 different wave vectors are used in the program presented. Sums over only 21 wave vectors are hardly

integrals over all wave vectors. This compromise leads to "ghost" packets which image the main packet but lie at large positive and negative x. The compromise also means that the packet shape is only approximate. This last program takes a long time to RUN. On some machines it is a half hour before the program finishes finding the spatial wave functions.

EXERCISES — Use computer when appropriate

I.   Using the fact (from Fourier Series calculations) that a triangle wave has only odd harmonics in the ratios of $1/(2n+1)^2$ n = 1, 2, 3, ... :

1. Set up such an initial electron distribution in an infinite square well.

2. Find the shape of the combination of states after 1 through 5 units of time.

3. Identify times when certain modes seem dominant. Explain this phenomenon in terms of the periods of the modes you used.

*II. Using the fact (from Fourier Series calculations) that a linear periodic wave (a ramp or sawtooth wave) has harmonic content in the ratios +1, –1/2, +1/3, –1/4, ... :

1. Set up such an initial electron distribution in an infinite square well.

2. Find the shape of the combination of states after 1 through 5 units of time.

3. Identify times when certain modes seem dominant. Explain this phenomenon in terms of the periods of the modes you used.

*III. Form a combination of the 3 lowest states of the infinite square well.

1. Find the form of your combination for T = 0, 1, 2, 9, and 16 units of time.

2. Is the motion periodic in time? What is (half) the lowest common multiple of the periods of the states?

IV. Form a Gaussian free wave packet at the origin at time equals zero. Use a central energy of 8 and a packet half-width of .5. See figure at right.

1. Propagate the wave packet for 0, .5, 1, 1.5, 2, and 2.5 units of time. Observe and discuss the behavior of the packet.

2. From your calculations, measure the group velocity of the wave packet. Compare this result to the central wave vector of the pulse and to the phase velocities for the lowest, highest, and central energy components of the packet.

3. From your calculations, measure the full-width at half maximum for the packet at each time. The width is predicted (for a Gaussian packet) to go as $W(t) = ((W(0))^2 + t^2/(W(0))^2)^{\frac{1}{2}}$. Do your measurements of the propagated packets agree?

4. By integrating (crudely) $|\Psi|^2$ across the whole range of x, see if the total probability for the particle remains constant.

*V. Form a triangular free wave packet at the origin at time equals zero. Use a central energy of 8 and a packet half-width of .5. See figure at right.

1. Propagate the wave packet for 0, .5, 1, 1.5, 2, and 2.5 units of time. Observe and discuss the behavior of the packet.

2. From your calculations, measure the group velocity of the wave packet. Compare this result to the central wave vector of the pulse and to the phase velocities for the lowest, highest, and central energy components of the packet.

3. From your calculations, measure the full-width at half maximum for the packet at each time. The width is predicted (for a Gaussian packet) to go as $W(t) = (W(0))^2 + t^2/(W(0)^2)^{1/2}$. Do your measurements of the propagated packets agree?

4. By integrating (crudely) $|\psi|^2$ across the whole range of x, see if the total probability for the particle remains constant.

*VI. Form a square free wave packet at the origin at time equals zero. Use a central energy of 8 and a packet half-width of .5.

1. Propagate the wave packet for 0, .5, 1, 1.5, 2, and 2.5 units of time. Observe and discuss the behavior of the packet.

2. From your calculations, measure the group velocity of the wave packet. Compare this result to the central wave vector of the pulse and to the phase velocities for the lowest, highest, and central energy components of the packet.

3. From your calculations, measure the full-width at half maximum for the packet at each time. The width is predicted (for a Gaussian packet) to go as $W(t) = ((W(0))^2 + t^2/(W(0)^2)^{1/2}$. Do your measurements of the propagated packets agree?

4. By integrating (crudely) $|\psi|^2$ across the whole range of x, see if the total proability for the particle remains constant.

**VII. Using a Gaussian wave packet (of central energy $E = 50$) and a Gaussian well (of depth 100 and half-width 1):

1. Propagate the packet for times of 0, .2, .4, .6, .8, and 1.

2. Describe and discuss the results in terms of reflection coefficients, transmission coefficients, and interference effects.

**VIII. Using a triangular wave packet (of central energy $E = 10$) and a Gaussian well (of depth 100 and half-width 1):

1. Propagate the packet for times of 0, 1, 2, 2.5, 3, 4, and 5.

2. Describe and discuss the results in terms of reflection coefficients, transmission coefficients, and interference effects.

CHAPTER FOUR: THREE-DIMENSIONAL CONTINUUM STATES FOR SPHERICALLY SYMMETRIC POTENTIALS

INTRODUCTION

With the computer you can solve for the continuum states of any spherically symmetric potential. The method is very similar to that described for calculating the discrete states for these potentials (Chapter Two). The three-dimensional time independent Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E\psi(\vec{r}) \tag{32}$$

As we did in Chapter Two, you can separate this differential equation into polar coordinates when V is spherically symmetric, i.e., when $V(\vec{r}) = V(r)$. You set $\psi(r) = R(r)Y(\theta,\phi)$ and substitute this expression into Equation (32). The result is (1) an equation for R(r) which includes the effective potential and the energy, and (2) an equation for $Y(\theta,\phi)$ are spherical harmonics:

$$Y_\ell^m(\theta,\phi) = N_{\ell m} \mathcal{L}_\ell^m(\cos\theta) e^{\pm im\phi} \tag{33}$$

where $N_{\ell m}$ is a normalization coefficient, ℓ and m are integers such that $|m| < = \ell$, and $\mathcal{L}_\ell^m$ is an associated Legendre function.

The equation for R(r) can be simplified by transforming to an equivalent for $P(r) = rR(r)$. The equation for P(r) looks very much like the one-dimensional Schrödinger equation:

$$\frac{d^2P(r)}{dr^2} = 2(V(r) + \ell(\ell+1)/(2r^2) - E)P(r) \tag{34}$$

This equation can be solved iteratively in the manner discussed in Chapters One and Two.

BOUNDARY CONDITIONS FOR P(r)

P(r) must go to zero smoothly as r goes to zero. This is just a consequence of the fact that R(r) must be bounded everywhere. If R(r) were infinite at some r_0, then $|\psi(r,\theta,\phi)|^2$ would also be infinite at that point. This would mean infinite probability of finding the particle at r_0 which is unphysical.

This demand that P(r) go to zero as r goes to zero demands that the solution for P(r) be unique. Hence, unlike the case of continuum states in one dimension (Chapter Three), there is only one radial wavefunction for each continuum energy in three dimensions.

If V(r) can be approximated by some simpler potential (for example, the Coulomb potential for the hydrogen atom) for small r, then you can approximate the behavior of R(r) in this region by that of the solutions to the simpler potential. Then the behavior of P(r) is also known for small r. (For the Coulomb case $P(r) \approx r^{\ell+1}$). This allows you to initialize the wave functions for such cases near r = 0 and then integrate step-by-step out to large r. When this is possible, it is the easiest strategy to use.

Assume now that V(r) goes to zero for large r. Most important, three-dimensional potentials do go to zero far enough from the force center. Then, as you can see from Equation (34), the form of the Schrödinger equation for P(r) becomes $P'' = -2EP$. The continuum states for such a potential have positive energies, E, so this equation for P has the (asymptotic) solution $P(r) = A\sin(kr) + B\cos(kr)$ for large r, $k = \sqrt{2E}$. Since there is only one state for each energy, we can conveniently write this solution as $P(r) = A\sin(kr - \ell\pi/2 + \delta_\ell)$ for large r. δ_ℓ is called the phase shift. The equation for R(r) at large r is then spherical Bessel functions, $R(r) = \sin(kr - \ell\pi/2 + \delta_\ell)/r$.

Notice there is no reason that P(r) should go to zero as r gets large. This is unlike the situation for discrete states; in discrete states, the wave function entered a classically forbidden region for large r, and P(r) had to go smoothly to zero. For continuum states, the only demand on R(r) and P(r) for large r is that they remain bounded.

THE ITERATIVE PROCEDURE

You can solve the equation for P(r) (Equation (34)) iteratively in much the same way we solved the same equation for discrete states in Chapter Two.

Suppose you know P(r) at some point r_1 and the behavior of P(r) somewhere else (say at r_2). You can initialize P(r) and P'(r) at r_1; you can then take a small step Δr towards r and find the next values of P and P' from

$$P(r+\Delta r) = P(r) + P'\left(r+\frac{\Delta r}{2}\right)\Delta r \tag{35}$$

$$P'(r+\Delta r) = P'(r) + P''\left(r+\frac{\Delta r}{2}\right)\Delta r \tag{36}$$

The value of P'' is obtained from Equation (34). The use of the half-step $(r+\Delta r/2)$ is discussed in the Appendix.

In this manner, you walk your way in (or out) r until you reach r_2. If the behavior at r_2 is correct, you have the state for that energy.

If you do not know the asymptotic expansion for P(r) near r = 0 (that is, if V(r) is not approximated by a potential whose solutions you know), then initialize P(r) to $\sin(kr-\ell\pi/2+\delta_\ell)$ at large r; integrate back to r = 0; and guess phase shifts, δ_ℓ, until you find the one for which P(r) goes smoothly to zero. One possible implementation of this strategy is:

```
SCAT1

 10  DEF FNV(R)=400*(R↑(-12)-R↑(-6))◄─── Potential, V(r)
 20  LET P=3.14159
 30  PRINT "R(START),R(END),DELTA-R?"
 40  INPUT R9,R8,R7
 50  PRINT "ORBITAL #(L),ENERGY,PHASE(DEGS.)?"
 60  INPUT L,E,D
 70  LET D=P*D/180                              ┐
 80  LET K=SQR(2*E)◄─── Wave vector             │ Initialization
 90  LET R7=-ABS(R7)                            │
100  LET P0=SIN(K*R8+D)                         │
110  LET P1=K*COS(K*R8+D)                       │
120  LET R=R9                                   │
130  LET N=0                                    ┘
140  PRINT R,P0,P0/R
150  LET R5=R9+(R8-R9)/20
160  LET R6=R+R7/2                              ┐
170  LET P2=2*(FNV(R6)+L*(L+1)/(2*R6*R6)-E)*(P0+P1*R7/2)  │ Integrate
180  LET P3=P0                                  │ Schrödinger
190  LET P0=P0+(P1+P2*R7/2)*R7                  │ equation
200  LET P1=P1+P2*R7                            │
210  LET R=R+R7                                 ┘
220  IF SGN(P0)=SGN(P3) THEN 260◄─── Test for zero crossing
230  LET N=N+1◄─── Count zero crossings
240  IF N>1 THEN 260
250  LET R0=((R-R7)*P0-R*P3)/(P0-P3) } Store asymptotic
260  IF R>R5 THEN 290                     zero crossing
270  LET R5=R5+(R8-R9)/20 } Print loop
280  PRINT R,P0,P0/R
290  IF R>R8 THEN 160◄─── Return for next Δr
300  LET P9=N*P-K*R0+L*P/2
310  PRINT "PHASE SHIFT (DEGS.) =";180*P9/P } Print phase shift, δ_ℓ
320  PRINT
330  GOTO 30◄─── Return for new parameters
340  END
```

The parts of the program dealing with phase shift calculations will be discussed in a section below on Scattering Theory.

If you do know the small r behavior of $P(r)$, then the solution is completely determined. You initialize the wave function $P(r)$ near $r = 0$ and integrate out to large r. You can then measure the phase shift, δ_ℓ, from the positions of zeros of P at large r. At a zero, r_0, in the large r region, $kr_0 - \ell\pi/2 + \delta_\ell = n\pi$, where n is the number of zeros of $P(r)$ between $r = 0$ and $r = r_0$; $k = \sqrt{2E}$. r_0 is measured so δ_ℓ can be calculated. $n\pi$ is the actual phase of the wave function at that zero; $kr_0 - \ell\pi/2$ is the phase the wave function would have if $V(r)$ were zero everywhere (i.e., when $P(r) = \sin(kr - \ell\pi/2)$ everywhere); so δ_ℓ is the phase shift of the true wave function relative to a free particle. Let's look at a specific problem—continuous states for the screened Coulomb potential, $V(r) = -\exp(-r/8)/r$.

CONTINUUM STATES FOR A SCREENED COULOMB POTENTIAL

You already know (before you start) a good deal about the solution. Since the potential is approximated by the unscreened Coulomb potential for small r, the wave function, P, comes out of $r = 0$ as $r^{\ell+1}$; the derivative then behaves as $(\ell+1)r^\ell$. At large r, $P(r)$ becomes a sine wave of constant amplitude. In this sine wave region, we will measure the phase shifts for a given energy and various orbital angular momentum quantum numbers, ℓ.

Find the wave function of the state with $E = 4$ and $\ell = 0$ using the computer.

A program implementing the strategy we just discussed follows:

```
SCAT2
10   DEF FNV(R)=-EXP(-R/8)/R  ◄——— Potential, V(r)
20   LET P=3.14159
30   PRINT "R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?"
40   INPUT R8,R9,R7,L,E
50   LET K=SQR(2*E)  ◄——— Wave vector
60   LET P0=R8↑(L+1)
70   LET P1=(L+1)*R8↑L
80   LET R=R8
90   PRINT R,P0,P0/R
100  LET N=0
110  LET R5=(R9-R8)/20
120  LET R6=R+R7/2
130  LET P2=2*(FNV(R6)+L*(L+1)/(2*R6*R6)-E)*(P0+P1*R7/2)
140  LET P3=P0
150  LET P0=P0+(P1+P2*R7/2)*R7
160  LET P1=P1+P2*R7
170  LET R=R+R7
180  IF SGN(P0)=SGN(P3) THEN 210  ◄——— Test for zero crossing
190  LET N=N+1  ◄——— Count zero crossings
200  LET R0=((R-R7)*P0-R*P3)/(P0-P3)  ◄——— Save last zero crossing
210  IF R<R5 THEN 240
220  LET R5=R5+(R9-R8)/20  ┐ Print loop
230  PRINT R,P0,P0/R       ┘
240  IF R<R9 THEN 120  ◄——— Return for new Δr step
250  LET P9=N*P-K*R0+L*P/2
260  PRINT "PHASE SHIFT (DEGS.) =";180*P9/P  ┐ Print phase
270  PRINT                                    ┘ shift, $\delta_\ell$
280  GOTO 30  ◄——— Return for new parameters
290  END
```

Annotations (right of code block):
- Initialization (brace covering lines 50–110)
- Integrate Schrödinger equation (brace covering lines 120–170)

```
SCAT2
R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?1E-8,20,.01,0,4
 1.00000E-08    1.00000E-08        1
 1.01          -.104641           -.103605
 2.01           8.31046E-02        4.13456E-02
 3.00002       -3.26691E-02       -1.08896E-02
 4.00004       -2.22426E-02       -5.56058E-03
 5.00007        8.03536E-02        1.60705E-02
 6.00009       -.135073           -2.25118E-02
 7.00011        .180357            2.57649E-02
 8.00014       -.21112            -2.63895E-02
 9.00016        .223709            2.48561E-02
 10.0002       -.216279           -2.16275E-02
 11.0002        .188997            1.71812E-02
 12.0002       -.144043           -1.20033E-02
 13.0002        .085408            6.56972E-03
 14.0003       -1.85095E-02       -1.32208E-03
 15.0003       -5.03436E-02       -3.35618E-03
 16.0003        .114574            7.16073E-03
 17.0001       -.16799            -9.88166E-03
 18.01          .202769            1.12587E-02
 19.0098       -.222403           -1.16994E-02
 20.0096        .22066             1.10277E-02
PHASE SHIFT (DEGS.) = 76.8723
R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?1E-8,20,.01,1,4
 1.00000E-08    1.00000E-16        1.00000E-08
 1.01           9.95304E-07        9.85450E-07
 2.01          -1.09195E-06       -5.43257E-07
 3.00002        1.11603E-06        3.72006E-07
 4.00004       -1.05106E-06       -2.62762E-07
 5.00007        8.99266E-07        1.79851E-07
 6.00009       -6.67755E-07       -1.11291E-07
 7.00011        3.73776E-07        5.33958E-08
 8.00014       -4.25069E-08       -5.31327E-09
 9.00016       -2.95826E-07       -3.28690E-08
 10.0002        6.09248E-07        6.09237E-08
 11.0002       -8.67447E-07       -7.88574E-08
 12.0002        1.04499E-06        8.70805E-08
 13.0002       -1.12398E-06       -8.64581E-08
 14.0003        1.09600E-06        7.82840E-08
 15.0003       -9.63026E-07       -6.42004E-08
 16.0003        7.37329E-07        4.60822E-08
 17.0001       -4.40326E-07       -2.59013E-08
 18.01          1.32242E-07        7.34273E-09
 19.0098        2.18111E-07        1.14736E-08
 20.0096       -5.47601E-07       -2.73668E-08
PHASE SHIFT (DEGS.) = 58.1795
R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?1E-8,20,.01,2,4
 1.00000E-08    1.00000E-24        1.00000E-16
 1.01           4.58785E-12        4.54243E-12
 2.01          -1.86842E-12       -9.29564E-13
 3.00002       -1.04727E-13       -3.49089E-14
 4.00004        1.69441E-12        4.23598E-13
 5.00007       -3.03941E-12       -6.07874E-13
 6.00009        4.06160E-12        6.76924E-13
 7.00011       -4.68043E-12       -6.68622E-13
 8.00014        4.84206E-12        6.05247E-13
 9.00016       -4.53217E-12       -5.03565E-13
 10.0002        3.78059E-12        3.78053E-13
 11.0002       -2.65989E-12       -2.41803E-13
 12.0002        1.27886E-12        1.06570E-13
 13.0002        2.27821E-13        1.75243E-14
 14.0003       -1.71282E-12       -1.22342E-13
 15.0003        3.03065E-12        2.02040E-13
 16.0003       -4.05205E-12       -2.53248E-13
 17.0001        4.67676E-12        2.75101E-13
 18.01         -4.84794E-12       -2.69181E-13
 19.0098        4.58227E-12        2.41047E-13
 20.0096       -3.86771E-12       -1.93292E-13
PHASE SHIFT (DEGS.) = 58.2172
R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?1E-8,20,.01,3,4
 1.00000E-08    1.00000E-32        1.00000E-24
 1.01           9.29985E-18        9.20778E-18
 2.01           1.39632E-17        6.94686E-18
 3.00002       -1.87301E-17       -6.24333E-18
 4.00004        1.85072E-17        4.62674E-18
 5.00007       -1.57158E-17       -3.14311E-18
 6.00009        1.11726E-17        1.86208E-18
 7.00011       -5.51514E-18       -7.87864E-19
 8.00014       -6.24036E-19       -7.80032E-20
 9.00016        6.61040E-18        7.34476E-19
 10.0002       -1.18457E-17       -1.18455E-18
 11.0002        1.58172E-17        1.43790E-18
 12.0002       -1.81431E-17       -1.51190E-18
 13.0002        1.86081E-17        1.43137E-18
 14.0003       -1.71823E-17       -1.22728E-18
 15.0003        1.40227E-17        9.34829E-19
 16.0003       -9.45674E-18       -5.91034E-19
 17.0001        3.94849E-18        2.32262E-19
 18.01          1.42276E-18        7.89985E-20
 19.0098       -7.15816E-18       -3.76551E-19
 20.0096        1.21736E-17        6.08387E-19
PHASE SHIFT (DEGS.) = 46.7426
R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?
END
```

A terminal plot of this wave function can be obtained by using the subroutines in TTYPLO (as discussed in the Appendix). The changes you might make and a RUN are:

```
5 READ X8,X9,Y8,Y9
6 DATA 0,20,-.15,1
7 GOSUB 9000
8 LET X0=Y0=Z0=0
9 GOSUB 9100
90 LET Z0=1
91 LET X0=R
92 LET Y0=P0/R
93 GOSUB 9100
230 LET X0=R
231 LET Y0=P0/R
232 GOSUB 9100
270 GOSUB 9200
APPEND-TTYPLO

220 LET R5=R5+(R9-R8)/70
RUN
SCAT2

R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?1E-6,20,.01,0,4
PHASE SHIFT (DEGS.) = 76.8723
MAX Y= 1
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y1
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y            11
Y          1        11        11        1
Y0    1   1   1   1   11   1   11 11  111111  11111111111111111111111111111
Y           1    111     111     11      11
Y          11
Y   1  1
Y
  XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y=-.15   MIN X= 0                    MAX X= 20
R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?
END
```

SCATTERING THEORY

The presence of a potential V(r) modifies the wave function (compared to the wave function for the free particle). Scattering theory deals with the phase shifts in terms of the differential and total cross sections. $\sigma(\theta)$ and σ_{tot}. Using the ideas developed in the last section, you can use the computer to find these phase shifts and cross sections for general, spherically symmetric potentials.

First, (to make clear the meaning of the phase shift) let's RUN the program for a continuum state of the free particle (V = 0 everywhere). You are actually producing the free particle wave function as expanded in polar coordinates. The radial function R(r) will be a spherical Bessel function.

We can use the program which initializes the wave function and its derivative at small r. For $\ell = 0$ the differential equation for P is $P'' = -2EP$ which gives the only acceptable solution, $P = A\sin(kr)$ where $k = \sqrt{2E}$. This solution is true everywhere so we already know that $R(r) = A\sin(kr)/r$ for $\ell = 0$ states. Notice that the small r behavior of P is $P \sim r^{\ell+1}$.

For $\ell >= 1$, the Schrödinger equation for P becomes for small r

$$P''(r) = (\ell(\ell+1)/r^2)P(r) \tag{37}$$

The solution for P has $P \sim r^{\ell+1}$. So these solutions can be initialized at small r to $P \sim r^{\ell+1}$, $P' \sim (\ell+1)r^{\ell}$. (These are the same arguments necessary to justify this initialization for the Coulomb potential; these arguments work for any potential which is dominated by the angular momentum term, $\ell(\ell+1)/(2r^2)$, at small r.)

A RUN of the program for V = 0, E = 4, and $\ell = 0$ is:

```
GET-SCAT2
10 DEF FNV(R)=0
RUN
SCAT2

R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?1E-8,20,.01,0,4
 1.00000E-08    1.00000E-08     1
 1.01           9.93218E-02     9.83384E-02
 2.01          -.198986        -.098998
 3.00002        .285323         9.51069E-02
 4.00004       -.335738        -8.39335E-02
 5.00007        .353513         7.07017E-02
 6.00009       -.336922        -5.61528E-02
 7.00011        .287577         4.10817E-02
 8.00014       -.210275        -2.62839E-02
 9.00016        .11253          1.25031E-02
 10.0002       -3.84594E-03    -3.84587E-04
 11.0002       -.105212        -9.56454E-03
 12.0002        .204042         1.70031E-02
 13.0002       -.283035        -2.17715E-02
 14.0003        .334514         2.38934E-02
 15.0003       -.353472        -2.35643E-02
 16.0003        .338867         2.11288E-02
 17.0001       -.289797        -1.70467E-02
 18.01          .221241         1.22843E-02
 19.0098       -.125566        -6.60533E-03
 20.0096        1.76845E-02     8.83797E-04
PHASE SHIFT (DEGS.) = .164799

R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?
END
```

A terminal plot of this state is:

```
10 DEF FNV(R)=0
RUN
SCAT2

R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?1E-8,20,.01,0,4
PHASE SHIFT (DEGS.) = .164799
MAX Y= 1
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Y I
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y
Y          I
Y      I   I I       I
Y           I I     III    II     II    I      I
Y0       I    I   I  II  II  II  II II III III IIIIIIIIIIIII
Y      I          III    II     II     II      I
Y         III
Y    I
Y     I
Y
Y
 XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
MIN Y=-.25   MIN X= 0                        MAX X= 20
R(START),R(END),DELTA-R,ORBITAL #(L),ENERGY?
?
END
```

You can see the relationship between the $V = 0$, $\ell = 0$ state and the $\ell = 0$ state shown before for the screened Coulomb potential. First, the behavior of $R(r)$ at small r is very s-state-like for the screened Coulomb potential; the small r region is very reminiscent of the discrete spectrum s states for this potential. Second, there is a clear phase shift between the free particle and the screened Coulomb wave functions at large r. This difference in phase is the phase shift, δ_ℓ, so central to scattering theory.

You can calculate δ_ℓ directly from your results: Count the number, n, of zero crossings of the wave function between the origin and some zero crossing at r_0 in the asymptotic region. The phase shift, δ_ℓ, is defined in scattering theory by setting the asymptotic behavior of $P(r) = A \sin(kr - \ell\pi/2 + \delta_\ell)$, where $k = \sqrt{2E}$. $(kr - \ell\pi/2)$ would be the phase of the free particle at r_0 so $\delta_\ell = n\pi - kr_0 + \ell\pi/2$.

Scattering theory points out that you can measure the shape of a potential by observing the interference pattern between a particle scattered off the potential and free particles which were not scattered. The parameters which are important in the interference pattern are the phase shifts, δ_ℓ, defined above.

In scattering theory, you write the asymptotic wave function as $f(\theta) \exp(ikr)/r$. The differential scattering cross section, $\sigma(\theta)$, is then $\sigma(\theta) = |f(\theta)|^2$. By expanding everything in spherical harmonics you find that

$$f(\theta) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell+1) \exp(i\delta_\ell) \sin\delta_\ell \, \mathcal{L}_\ell(\cos\theta)$$

where δ_ℓ is the phase shift and $\mathcal{L}_\ell(\cos\theta)$ is the ℓth Legendre polynomial; k is still $\sqrt{2E}$.

You can calculate the Legendre polynomials most easily by using the recursion relation

$$\ell\mathcal{L}_\ell(\cos\theta) = (2\ell-1)\cos\theta\,\mathcal{L}_{\ell-1}(\cos\theta) - (\ell-1)\mathcal{L}_{\ell-2}(\cos\theta)$$

with the two lowest order polynomials, $\mathcal{L}_0 = 1$ and $\mathcal{L}_1 = \cos\theta$.

A program to do this calculation (and its RUN) might look like:

```
10    PRINT "ANGLE (DEGS.)?"
20    INPUT T
30    LET T=3.14159*T/180
40    LET C=COS(T)
50    LET L0=1                              ← 𝓛₀
60    PRINT " 0",L0
70    LET L1=C                              ← 𝓛₁
80    PRINT " 1",L1
90    FOR L=2 TO 10
100   LET L2=((2*L-1)*C*L1-(L-1)*L0)/L      ← Recursion relation for 𝓛ℓ
110   PRINT L,L2
120   LET L0=L1
130   LET L1=L2
140   NEXT L
150   PRINT
160   GOTO 10                               ← Return for new angle
170   END

END
RUN
LEGEN

ANGLE (DEGS.)?
?45
0                      1
1                       .707107
2                       .250001
3                      -.176776
4                      -.40625
5                      -.375651
6                      -.148439
7                       .127057
8                       .29834
9                       .285536
10                      .115114
```

You can measure the phase shifts, δ_ℓ, for a given potential and given energy from your computer-based calculation of P(r). You can calculate the Legendre polynomials using the program given earlier. Finally, you can calculate $f(\theta)$ and, from $f(\theta)$, $\sigma(\theta)$, the differential cross section.

You can calculate the total cross section, σ_{tot}, even more easily. The total cross section (from scattering theory) is given by

$$\sigma_{tot} = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2 \delta_\ell$$

σ_{tot} is very easily measured from the computer derived phase shifts.

To calculate cross sections you need to calculate phase shifts for a number of orbital angular momentum quantum numbers, ℓ. You need phase shifts for all ℓ up to that for which the phase shift is negligibly small. Scattering theory suggests that, if R is a characteristic radius of the potential, then: when $kR \gg 1$, δ_ℓ's for all ℓ are needed; when $kR \ll 1$, only δ_0 and δ_1 are important, $k = \sqrt{2E}$. This fact makes these calculations well suited to individual project work. You could also divide up the different ℓ states and have some people find certain phase shifts and other people find others. Everyone can then use all the results to derive cross section information.

The simplest way to calculate phase shifts using the continum wave function program is to remove the lines which print out the wave functions. Since phase is very sensitive to small inaccuracies in the calculation, the phase shifts are only good to a few degrees. You can check the method by calculating phase shifts for V = 0 everywhere. You could use a higher convergence method for more accuracy. You would still need to integrate far out to get the phase of the asymptotic wave function correct. Even for V = 0 (excluding $\ell = 0$), you must integrate far enough out to make $\ell(\ell+1)/(2r^2)$ completely negligible with respect to the energy. Notice that, if V(r) becomes negligible then both the free particle and the particle in V(r) are obeying $P'' = 2(\ell(\ell+1)/(2r^2)-E)P$. You can get an approximation to the phase shift by comparing the phases of the V = 0 and V(r) particles when V(r) is negligible (even though neither solution is truly in its asymptotic region).

For example, find the ℓ = 0, 1, 2, and 3 phase shifts for the screened Coulomb potential $V(r) = -\exp(-r/8)/r$. Use an energy, E, of 4.

The results of RUNing the program are:

$$\delta_0 = 76.8 - 0.1 = 76.7; \ \delta_1 = 58.2 - 1.1 = 57.1;$$

$$\delta_2 = 50.2 - 3.1 = 47.1; \ \delta_3 = 46.7 - 6.4 = 40.3$$

If we take the screening parameter, 8, as the measure of the size, R, of the potential, then, for E = 4, kR = 22.6 which is large with respect to ℓ. We expect to need a large number of ℓ to produce a good approximation to the cross sections. Other kR are illustrated in the exercises.

Now let's calculate an approximation to the total cross section using the 4 phase shifts calculated above.

A program to combine the phase shifts into cross sections might look like:

```
CROSS
10    PRINT "MAX. L, ENERGY, ANGLE (DEGS.)?"
20    INPUT N,E,A
30    LET A=A*3.14159/180
40    LET K=SQR(2*E)        ←—— Wave vector
50    LET C=COS(A)
60    LET S1=F1=F2=0
70    PRINT "DELTA FOR EACH L (DEGS.)?"
80    FOR L=0 TO N
90    PRINT "L=";L
100   INPUT D
110   LET D=D*3.14159/180
120   IF L=0 THEN 180
130   IF L=1 THEN 200
140   LET L2=((2*L-1)*C*L1-(L-1)*L0)/L  ←—— £ℓ by recursion
150   LET L0=L1
160   LET L1=L2
170   GOTO 210
180   LET L0=L2=1  ←—— £0
190   GOTO 210
200   LET L1=L2=C  ←—— £1
210   LET S=SIN(D)
220   LET F1=F1+(2*L+1)*COS(D)*S*L2  ←—— Real part of f(θ)
230   LET F2=F2+(2*L+1)*S*S*L2  ←—————— Imaginary part
240   LET S1=S1+(2*L+1)*S*S  ←——————— Total cross section
250   NEXT L
260   PRINT "F(THETA)="
270   PRINT F1/K,F2/K
280   PRINT "SIGMA(THETA)="
290   PRINT (F1*F1+F2*F2)/(K*K)
300   PRINT "SIGMA TOTAL="
310   PRINT 4*3.14159*S1/(K*K)
320   PRINT
330   GOTO 10  ←—— Return for new parameters
340   END
```

{ Initialization }

Finally, let's calculate an approximation to the differential cross section, $\sigma(\theta)$ at $\theta = 0$ degrees.

```
MAX. L, ENERGY, ANGLE (DEGS.)?
?3,4,0
DELTA FOR EACH L (DEGS.)?
L= 0
?76.7
L= 1
?57.1
L= 2
?47.1
L= 3
?40.3
F(THETA)=
 2.66521        3.06652
SIGMA(THETA)=
 16.5069
SIGMA TOTAL=
 13.6242

MAX. L, ENERGY, ANGLE (DEGS.)?
?
END
```

EXERCISES — Use computer when appropriate.

I. For the potential, $V(r) = -\exp(-r/8)/r$, and an energy of $E = 10$:

1. Plot the effective potential for $\ell = 0, 1, 2,$ and 3. What is kR for this situation?

2. Plot the radial wave function for $\ell = 0$ and $\ell = 1$.

3. Find the phase shifts for $\ell = 0, 1, 2,$ and 3.

4. Calculate an approximation to the differential cross section at 0, 90, and 180 degrees using the four phase shifts from Part 3.

5. Calculate an approximation to the total cross section using these four phase shifts.

Hint: Use the program which initializes the wave function at small r. To get better accuracy for the phase shifts, subtract the corresponding values of the phase shifts for $V = 0$.

II. For the potential, $V(r) = -\exp(-r/8)/r$, and an energy of $E = 1$:

   1. Plot the effective potential for $\ell = 0, 1, 2,$ and 3. What is kR for this situation?

   2. Plot the radial wave function for $\ell = 0$ and $\ell = 1$.

   3. Find the phase shifts for $\ell = 0, 1, 2,$ and 3.

   4. Calculate an approximation to the differential cross section at 0, 90, and 180 degrees using the four phase shifts from Part 3.

   5. Calculate an approximation to the total cross section using these four phase shifts.

   Hint: Use the program which initializes the wave function at small r. To get better accuracy for the phase shifts, subtract the corresponding values of the phase shifts for $V = 0$.

III. For the potential, $V(r) = -\exp(-r/.5)/r$, and an energy of $E = 1$:

   1. Plot the effective potential for $\ell = 0, 1, 2,$ and 3. What is kR for this situation?

   2. Plot the radial wave function for $\ell = 0$ and $\ell = 1$.

   3. Find the phase shifts for $\ell = 0, 1, 2,$ and 3.

   4. Calculate an approximation to the differential cross section at 0, 90, and 180 degrees using the four phase shifts from Part 3.

   5. Calculate an approximation to the total cross section using these four phase shifts.

   Hint: Use the program which initializes the wave function at small r. To get better accuracy for the phase shifts, subtract the corresponding values of the phase shifts for $V = 0$.

*IV. For the potential, $V(r) = 400(1/r^{12} - 1/r^6)$, and an energy of $E = 1$:

   1. Plot the effective potential for $\ell = 0, 1, 2,$ and 3. What is kR for this situation?

   2. Plot the radial wave function for $\ell = 0$ and $\ell = 1$.

   3. Find the phase shifts for $\ell = 0, 1, 2,$ and 3.

   4. Calculate an approximation to the differential cross section at 0, 90, and 180 degrees using the four phase shifts from Part 3.

   5. Calculate an approximation to the total cross section using these four phase shifts.

   Hint: Use the program which initializes the wave function at large r.

**V. For the family of (Mie) potentials, $V(r) = 100(1/r^m - 1/r^n)$:

   1. Find the $(\ell = 0, E = 1)$ and $(\ell = 1, E = 1)$ phase shifts for $m = 12$ and $n = 1, 2,$ and 6. Disucss how the behaviors of δ_0 and δ_1 reflect the shape of the potential.

2. Now write the potential as $V(r) = 100((r_0/r)^{12} - (r_0/r)^6)$. Find the $(\ell = 0, E = 1)$ phase shifts, δ_0, for $r_0 = 1, 4, 8,$ and 16. Compare the results to δ_0 from Part 1. Discuss how the behavior of δ_0 reflects the characteristic diameter of the potential.

Hint: Use the program which initializes the wave function at large r.

*VI. For the family of potentials, $V(r) = -\exp(-r/r_0)/r$:

1. Find the $\ell = 0, E = 1$ phase shift for $r_0 = .1, .5, 1, 5,$ and 10. Discuss how the behavior of δ_0 reflects the screening.

2. Find the $\ell = 1, E = 1$ phase shift for $r_0 = .1, .5, 1, 5,$ and 10. Discuss how the behavior of δ_1 reflects the screening.

APPENDIX

INTRODUCTION

This appendix covers several topics: the terminal plotting performed by the subroutines in TTYPLO, the proof that symmetry of a one-dimensional potential (for potentials which are finite for finite x) determines that the states can be written as wholly even or wholly odd, and a short discussion of the half-step method of iterative integration.

TERMINAL PLOTTING

The subroutines in TTYPLO (listed below) allow you to plot a set of curves on your terminal. The subroutines use the O variables, so you should not use these variables in your programs. The output from the subroutines is a 7" by 5" x-y plot (assuming 6 lines/inch and 10 characters/inch) with the x-axis across the page and the y-axis up the page.

You set the range of x values on the plot by defining values for X8 = the left side of the plot, X9 = the right side of the plot, Y8 = the bottom of the plot, and Y9 = the top of the plot. You then call the subroutines with "GOSUB 9000."

To plot a point on the graph, you define the values of X0 = the x coordinate and Y0 = the y coordinate of the point. You also specify a value for Z0, which will be the character plotted at the point (X0, Y0) on the graph. You then call "GOSUB 9100." The allowed values of Z0 are 0 throuth 9. Since these variables X8, X9, Y8, Y9, X0, Y0, Z0 are used in these special ways for the plotting, you should be careful how you use them in your programs.

To product the final plot on your terminal, you call "GOSUB 9200."

A sample of the use of TTYPLO follows. The program plots a sine curve (as the character "1") and a cosine curve (as the character "2").

```
10 READ X8,X9,Y8,Y9        ⎫
20 DATA 0,6.28318,-1,1     ⎬ Initialize plot
30 GOSUB 9000              ⎭
40 FOR X0=X8 TO X9 STEP (X9-X8)/70 ◄── Step across angle
50 LET Z0=1
60 LET Y0=SIN(X0)          ⎫ Store sine in plot
70 GOSUB 9100              ⎭
80 LET Z0=2
90 LET Y0=COS(X0)          ⎫ Store cosine in plot
100 GOSUB 9100            ⎭
110 NEXT X0
120 GOSUB 9200 ◄── Print out plot
130 STOP
APPEND-TTYPLO ◄── Add plotting subroutines to program
```

MAX Y= 1

A LISTing of TTYPLO gives:

```
9000    REM INITIALIZE PLOT
9010    DIM O[300]
9020    FOR O1=1 TO 300
9030    LET O[O1]=0
9040    NEXT O1
9050    LET O[76]=76
9060    RETURN
9100    REM STORE POINTS
9110    IF (X0-X8)*(X0-X9)>0 THEN 9190
9120    IF (Y0-Y8)*(Y0-Y9)>0 THEN 9190
9130    LET O[76]=O[76]+1
9140    LET O[O[76]]=1000*INT(30*(Y0-Y8)/(Y9-Y8)+1.5)
9150    LET O[O[76]]=O[O[76]]+10*INT(70*(X0-X8)/(X9-X8)+1.5)+Z0
9160    IF O[76]<300 THEN 9190
9170    PRINT "PART OF THE PICTURE NOW"
9180    GOTO 9200
9190    RETURN
9200    REM PRINT OUT PLOT
9210    PRINT "MAX Y=";Y9
9220    PRINT " XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
9230    FOR O2=31 TO 1 STEP -1
9240    FOR O3=1 TO 75
9250    LET O[O3]=-1
9260    NEXT O3
9270    LET O6=0
9280    FOR O3=77 TO O[76]
9290    IF O[O3]<0 THEN 9360
9300    IF INT(O[O3]/1000) <> O2 THEN 9360
9310    LET O1=O[O3]-1000*INT(O[O3]/1000)
9320    LET O[INT(O1/10)]=O1-10*INT(O1/10)
9330    IF O6>INT(O1/10) THEN 9350
9340    LET O6=INT(O1/10)
9350    LET O[O3]=-1
9360    NEXT O3
9370    PRINT "Y";
9380    FOR O3=1 TO O6
9390    GOTO O[O3]+2 OF 9400,9420,9440,9460,9480,9500,9520,9540,9560,9580
9400    PRINT " ";
9410    GOTO 9610
9420    PRINT "0";
9430    GOTO 9610
9440    PRINT "1";
9450    GOTO 9610
9460    PRINT "2";
9470    GOTO 9610
9480    PRINT "3";
9490    GOTO 9610
9500    PRINT "4";
9510    GOTO 9610
9520    PRINT "5";
9530    GOTO 9610
9540    PRINT "6";
9550    GOTO 9610
9560    PRINT "7";
9570    GOTO 9610
9580    PRINT "8";
9590    GOTO 9610
9600    PRINT "9";
9610    NEXT O3
9620    PRINT
9630    NEXT O2
9640    PRINT " XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
9650    PRINT "MIN Y=";Y8;"    MIN X=";X8," ","MAX X=";X9
9660    GOSUB 9000
9670    RETURN
9680    END
```

Annotations (right margin):
- *Initialize the storage vector* (lines 9000–9050)
- *Test for offscale points* (9110, 9120)
- *Count points plotted* (9130)
- *Store X0, Y0, Z0 in one element of storage vector* (9140, 9150)
- *Test for too many points* (9160)
- *Print out picture* (9180)
- *Step down page* (9230)
- *Initialize line* (9240, 9250)
- *Step through stored points* (9280)
- *Test for unused or already used elements* (9290)
- *Is element in this line?* (9300)
- *Remove Y0 to get X0* (9310)
- *Remove X0 to get Z0* (9320)
- *Find largest X0 in line* (9330)
- *Reset element* (9350)
- *Step across line* (9380)
- *Print correct character (Z0) at each position*
- *Re-initialize plot* (9660)

SYMMETRY PROOF FOR ONE–DIMENSIONAL POTENTIALS

If the potential is symmetric, then the probability density (the probability per unit length), $|\psi|^2$, will also be symmetric, i.e., $|\psi(-x)|^2 = |\psi(x)|^2$. When the wave function is real (which usually just means "when the potential is real"), we have that

$$\psi(-x) = \pm \psi(x) \qquad (A1)$$

as the only possibilities. If ψ were a mixture of some even and some odd, then $|\psi|^2$ would not be symmetric. Hence the wave functions can be written as wholly even ($\psi(-x) = \psi(x)$) or wholly odd ($\psi(-x) = -\psi(x)$). If there is only one wave function for a certain energy, E, then that wave function must be either even or odd; it cannot be a mixture.

A more mathematical proof goes as follows:

Consider a potential, V, such that $V(-x) = V(x)$. Define an operator, P, called the *parity* operator, by $P[f(x)] = f(-x)$.

1. The parity operator is Hermitian.

$$\int_{-\infty}^{\infty} \psi^*(x) P[\psi(x)] \, dx = \int_{-\infty}^{\infty} (P[\psi(x)])^* \psi(x) \, dy$$

where * means complex conjugate.

2. The eigenvalues of the parity operator are +1 and –1.

$$P[\psi(x)] = \alpha\psi(x)$$

$$P^2[\psi(x)] = \alpha P[\psi(x)] = \alpha^2 \psi(x)$$

But $P^2[f(x)] = P[f(-x)] = f(x)$ for any f

Hence $\alpha^2 = 1$ or $\alpha = +1$ or -1

3. The eigen functions of the parity operator are even and odd.

From 2: $P[\psi(x)] = \psi(x)$ or $P[\psi(x)] = -\psi(x)$

for any eigen function

That means $\psi(-x) = \psi(x)$ or $\psi(-x) = -\psi(x)$

i.e., that the functions are even or odd, respectively.

4. Finally, then, the parity operator operating on the Schrödinger equation with a symmetric potential is the same as the Schrödinger equation for $\psi(-x)$.

This in turn implies that the eigen functions of the Schrödinger equation can be written as eigen functions of the parity operator.

THE HALF-STEP ITERATIVE INTEGRATION

Numerical methods are a subject in mathematics. You may want to study the subject someday. For the moment, all we need to show you is that the half-step method used heavily in Chapters One and Two would seem to give better answers than the simplest approximation (which is called Euler's method). The problem we're discussing is a general one. A physical law often can be stated in terms of the derivative of a function you wish to find; you integrate the differential equation to find the answer.

Consider a general curve for $y = f(x)$; suppose you know the value of y at $x = x_0$ and you have a way to calculate the derivative of y with respect to x anywhere. The problem is to get as good an approximation to the correct value $y = f(x_0+\triangle x)$ as reasonably possible. The simplest method (Euler's method) uses the derivative at x_0 and approximates $f(x_0+\triangle x)$ as $f(x_0+\triangle x) = f(x_0) + f'(x_0)\triangle x$.

Euler's method is shown on the sketch by the dashed line. Clearly, although in the limit as $x \to 0$ the method is correct, for finite $\triangle x$ the method is not very good.

The geometrical interpretation of the theorem which mathematicians call the Mean Value Theorem says that there is some point on the continuously differentiable curve $y = f(x)$ such that the derivative at that point has the same value as the slope of the chord from $(x_0, f(x_0))$ to $(x_0 + \Delta x, f(x_0 + \Delta x))$. If the theorem told us where that point was, everything would be easy. So-called higher order methods of iterative integration (such as the fourth-order Runge-Kutta method) are ways to approximate better and better this "correct" value of slope.

Our half-step method is based on the fact that, in general, evaluating the derivative near the center of the interval $(x_0, x_0 + \triangle x)$ is better than using a derivative at the end of the interval. In fact, you can show that, if $f(x)$ is a parabola, then a half-step method is exact. This means that, if you expand $f(x)$ around x_0 in a Taylor series, the half-step method will be correct through terms in $(\triangle x)^2$. That's why half-step methods are called "second-order" Runge-Kutta methods.
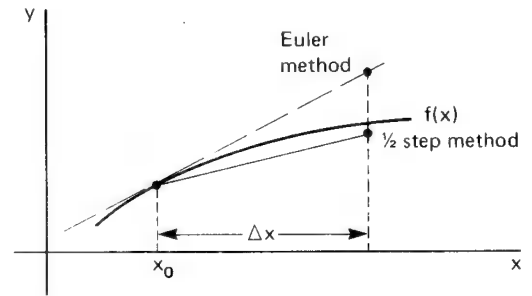
SELECTED ANSWERS

CHAPTER ONE

Exercise II. 2(a) E = 2.418
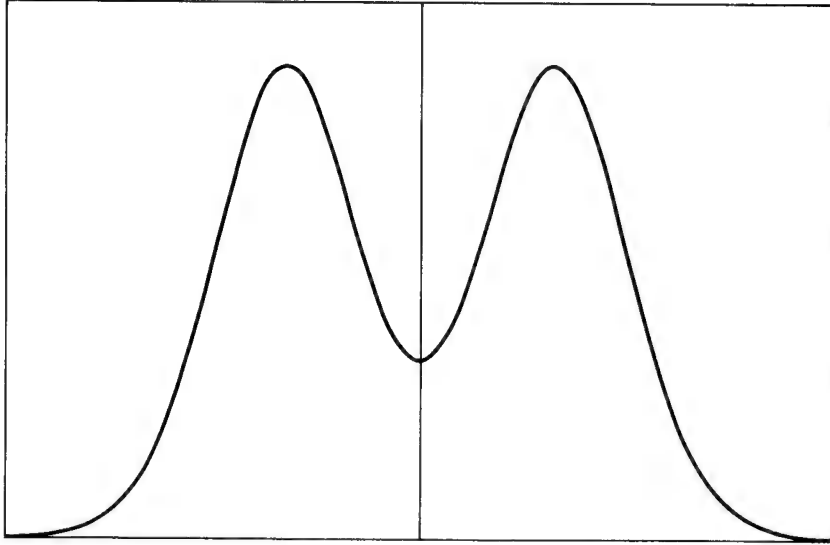
2(b) none (except t – ∞)

2(c) .224

2(d) 1.41

3(a) E = 2.507
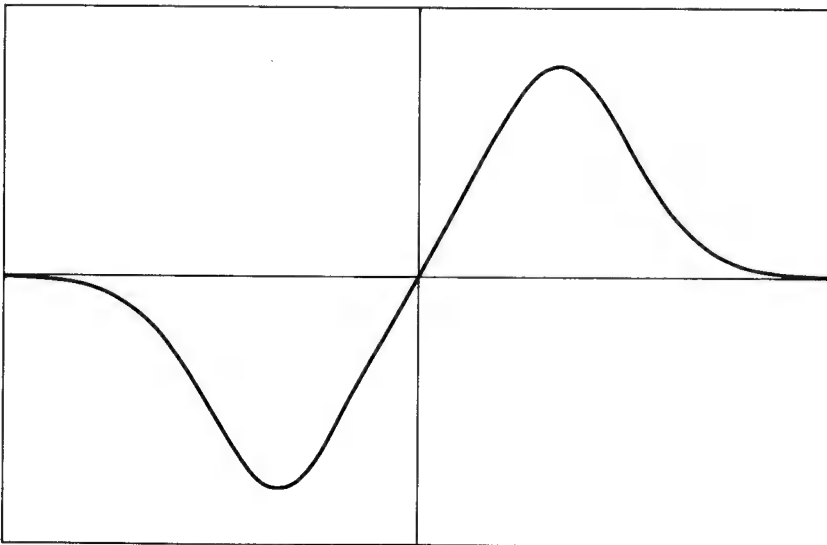
3(b) one (and + – ∞)

3(c) 0.389

3(d) 1.52

4. E = .089 a.u. = 2.42 eV = 3.88×10^{-12} ergs = 5.86×10^{14} Hertz = 5120Å.

Exercise III. 2(a) E = .6845
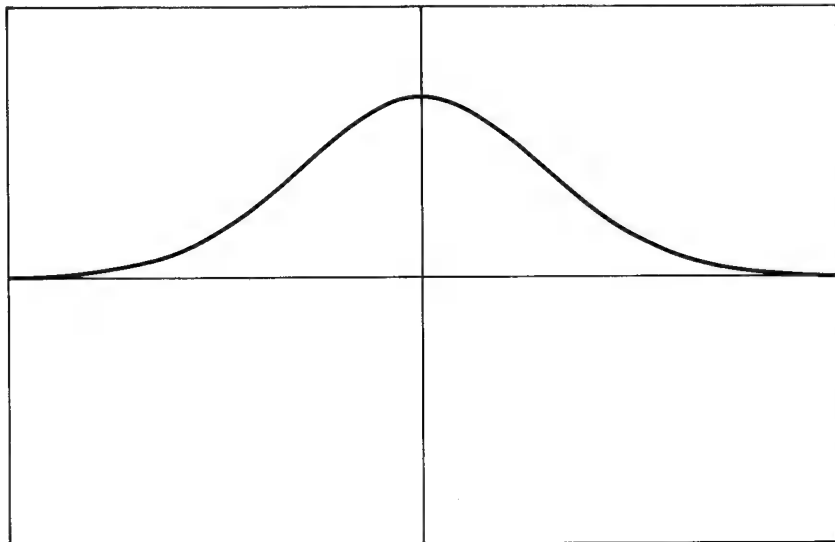
2(b) none (except + – ∞)

2(c) .812

2(d) .40

3(a) E = 2.008
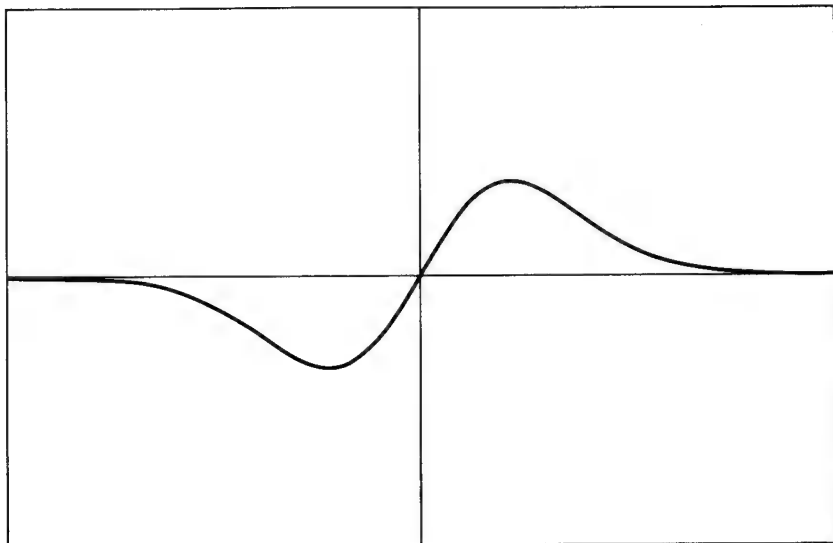
3(b) one (and $+-\infty$)

3(c) 1.294

3(d) 0.95

4. $E = 1.324$ a.u. $= 36.03$ eV $= 5.77 \times 10^{-11}$ ergs $= 8.71 \times 10^{15}$
Hertz $= 344$Å.

Exercise IV. 2(a) $E = -8.513$
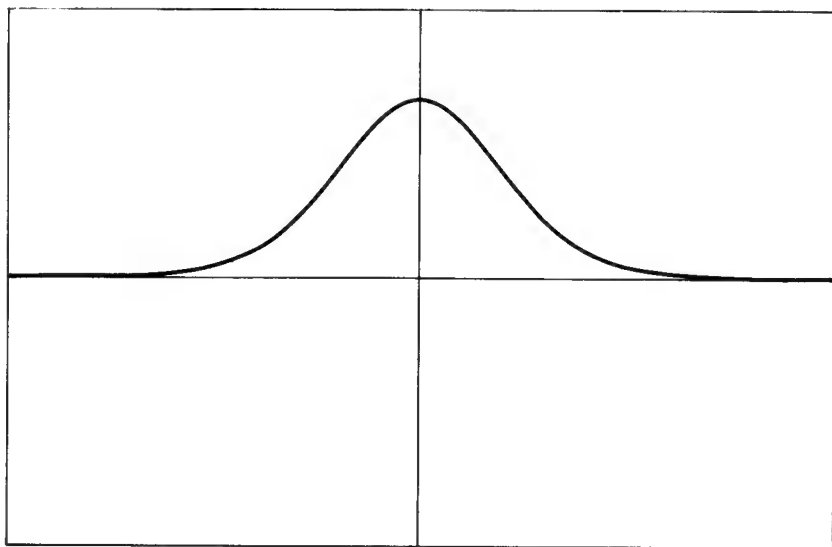
2(b) none (except $+-\infty$)

2(c) 0.983

2(d) 0.28

3(a) $E = -5.743$
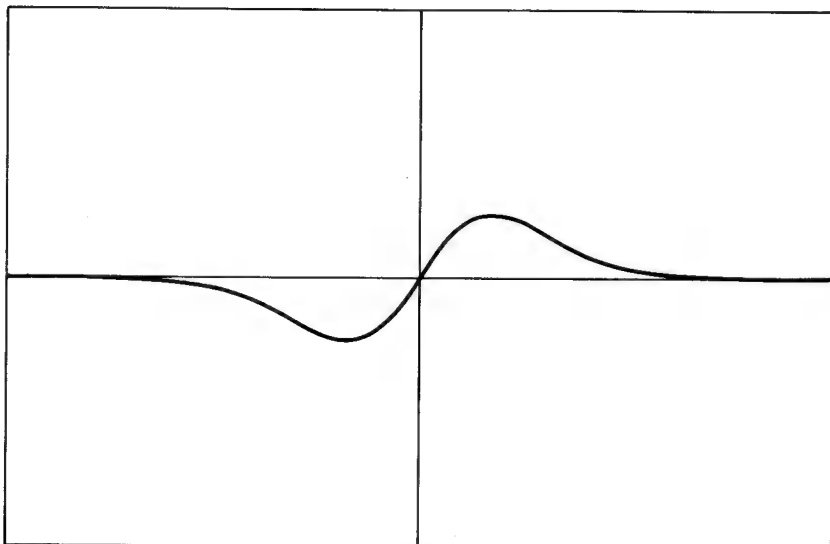
3(b) one (and + – ∞)

3(c) 2.214

3(d) 0.67

4. E = 2.76 a.u. = 75.1 eV = 1.20x10^{-10} ergs = 1.82x10^{16} Hertz = 165Å.
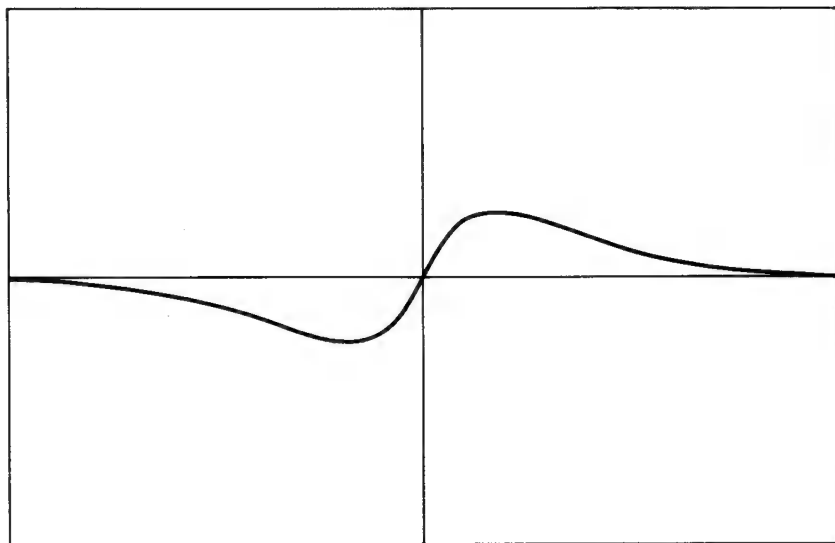
Exercise V. 2(a) E = –.407

2(b) one (and + – ∞)

2(c) 1.407

2(d) 1.33

3(a) E = –.0499
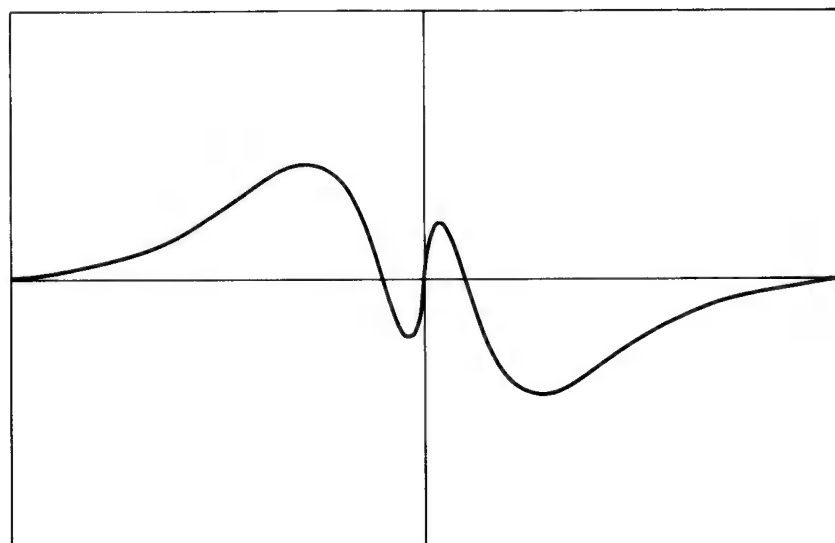
3(b) three (and + – ∞)

3(c) 0.452

3(d) 6.18

4. E = .370 a.u. = 10.1 eV = 1.61×10^{-11} ergs = 2.43×10^{15} Hertz = 1230 Å.

CHAPTER TWO

Exercise I. 2(a) E = –.407
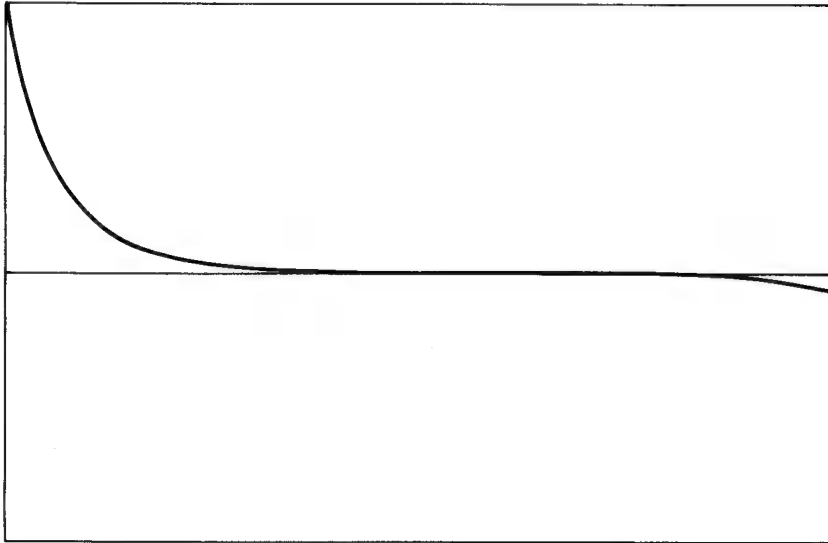
2(b) E = –.0499
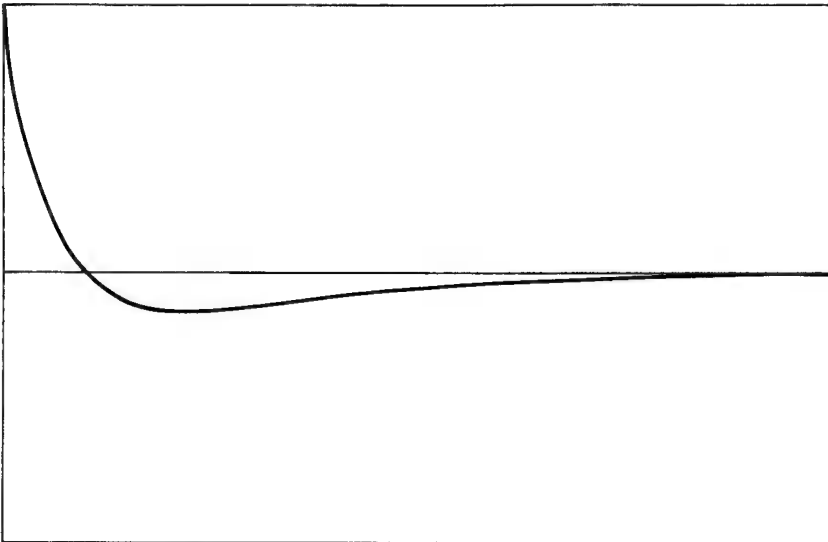
2(c)   E = –.0465
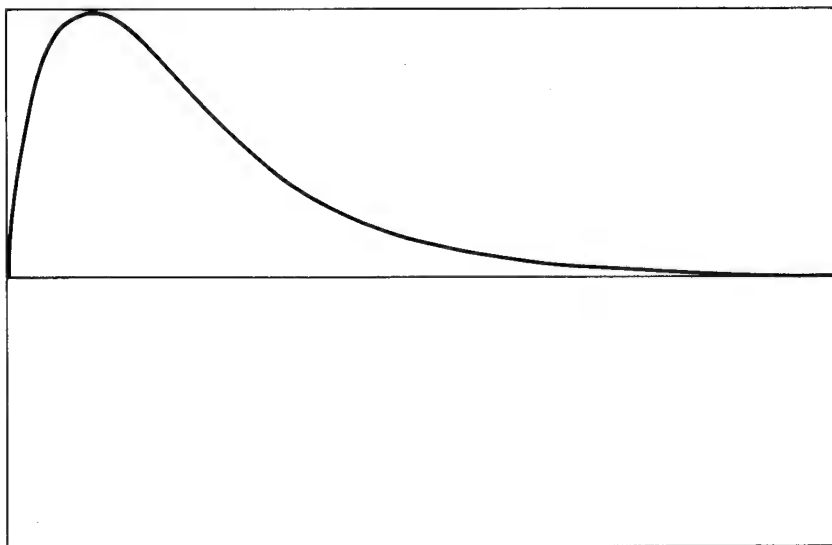
3. E = .357 a.u. = 9.71 eV = 1.56x10^{-11} ergs = 2.35x10^{15}
Hertz = 1280Å.

Exercise III. 2(a)   E = –.327
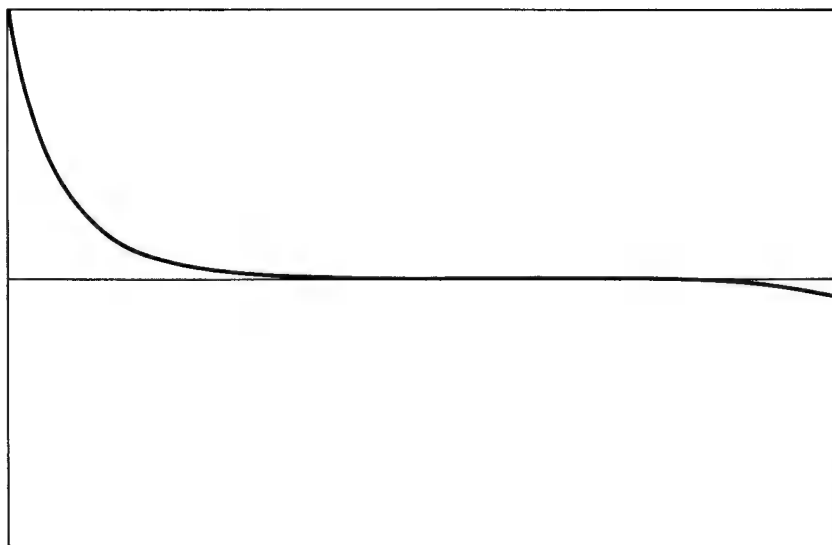
2(b) E = -.0113
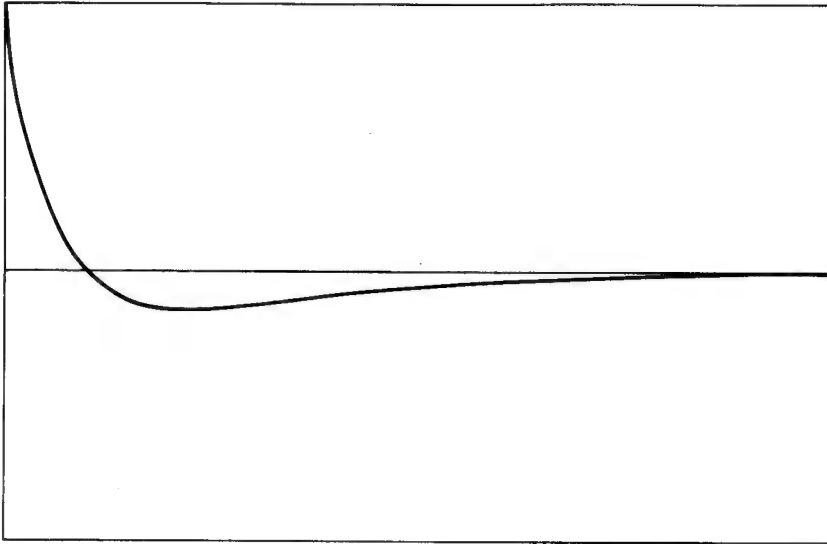
2(c) E = -.00399
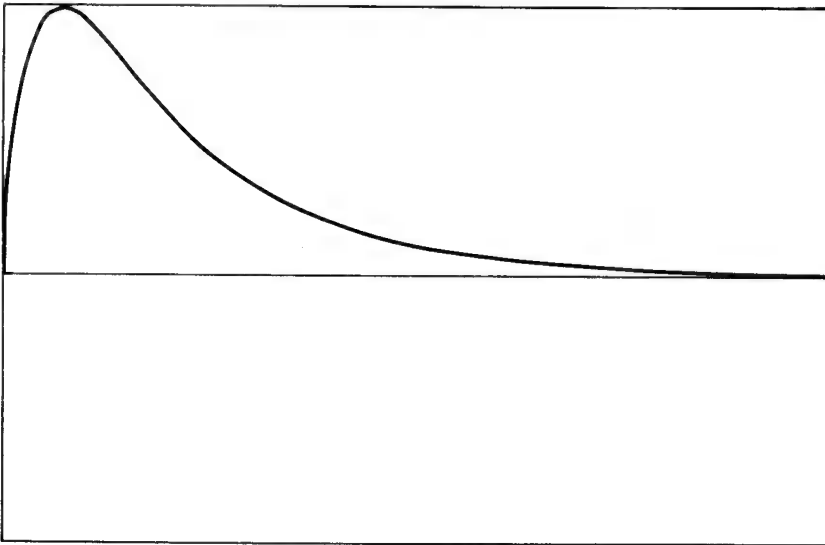
3. E = .316 a.u. = 8.60 eV = 1.38×10^{-11} ergs = 2.08×10^{15} Hertz = 1440Å.

Exercise III. 2(a) E = –66.27
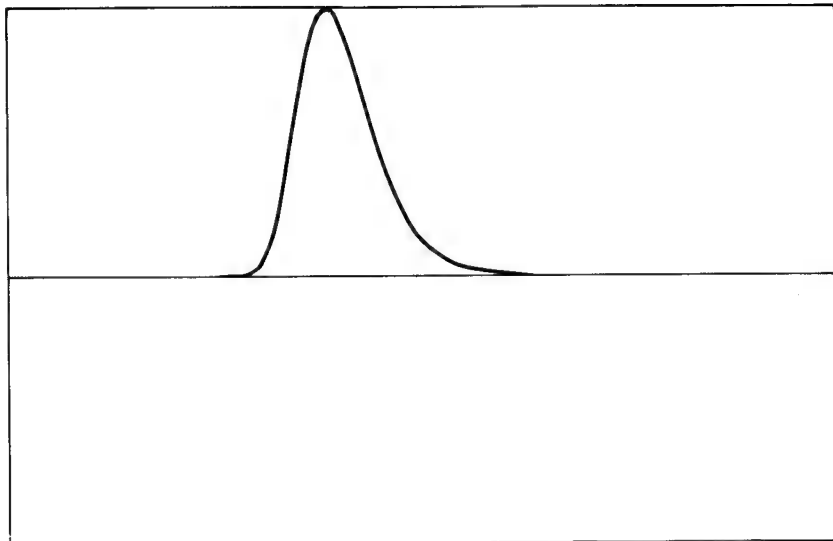
2(b) E = –22.98
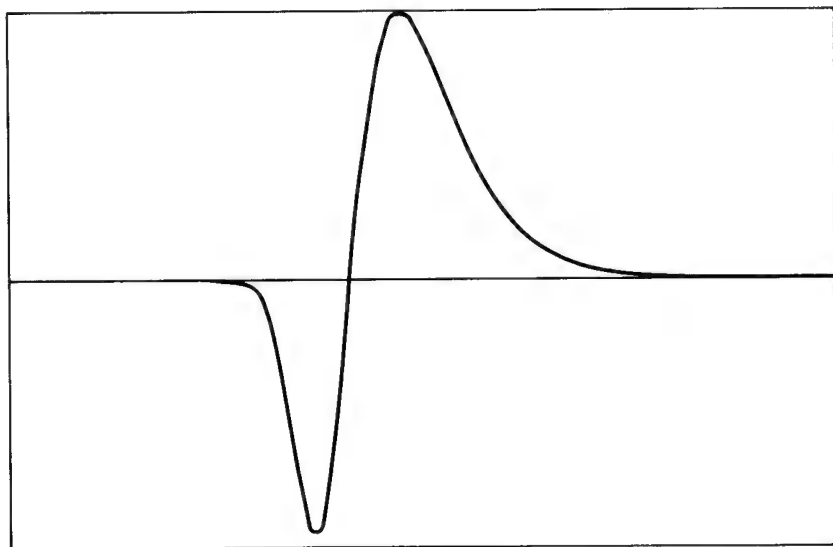
2(c) E = -22.44
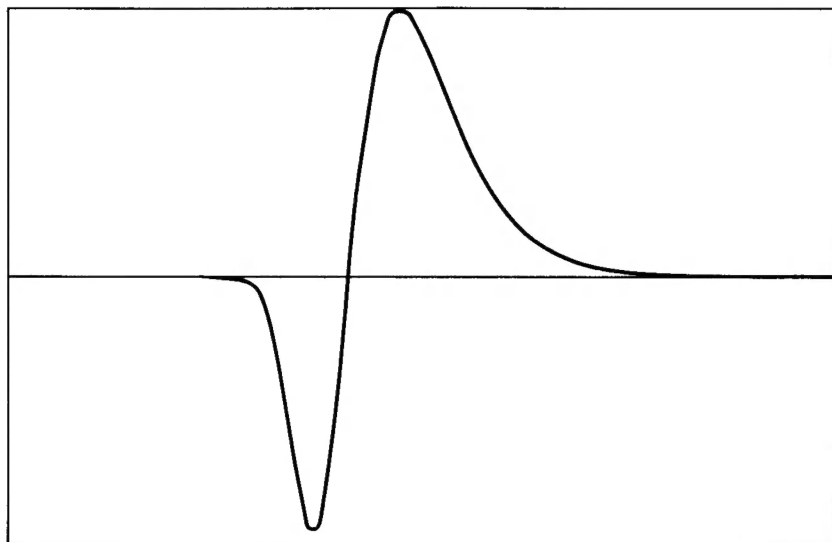
3. E = 43.29 a.u. = 1177 eV = 1.89×10^{-9} ergs = 2.85×10^{17} Hertz = 10.5Å.

Exercise IV. 2(a) E = -.0100
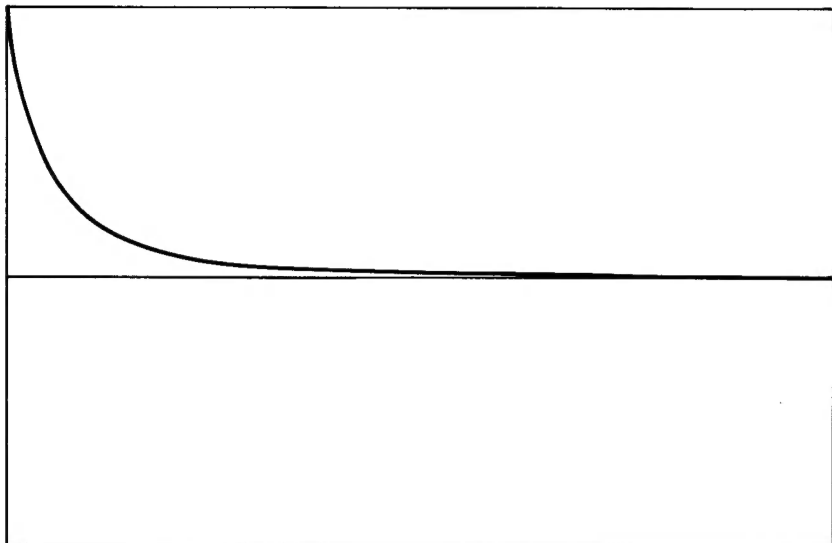
2(b) apparently lost to the continuum

2(c) apparently lost to the continuum

3. Since the second state is apparently in the continuum, you can set a lower bound on the energy difference.

E = .0100 a.u. = .272 eV = 4.36×10^{-13} ergs = 6.58×10^{13} Hertz = 45600 Å.

CHAPTER FOUR

Exercise I. 3. Integrating to 20:

δ_0 = 54.8 - 0.4 = 54.4 degrees

δ_1 = 42.8 - 1.1 = 41.7 degrees

δ_2 = 37.7 - 2.4 = 35.3 degrees

δ_3 = 35.4 - 4.2 = 31.4 degrees

4. $\sigma(0)$ = 4.31

$\sigma(90)$ = .0264

$\sigma(180)$ = .197

5. σ_{tot} = 3.49

Exercise II. 3. Integrating to 20:

δ_0 = 124.4 - 0 = 124.4 degrees

δ_1 = 90.1 - 2.2 = 87.9 degrees

δ_2 = 74.4 - 6.1 = 68.3 degrees

δ_3 = 68.2 - 13.0 = 55.2 degrees

4. $\sigma(0)$ = 91.6

$\sigma(90)$ = 1.97

$\sigma(180)$ = 5.98

5. σ_{tot} = 79.9

Exercise III. 3. Integrating to 20:

δ_0 = 29.3 - 0 = 29.3 degrees

δ_1 = 6.5 - 2.2 = 4.3 degrees

δ_2 = 7.0 - 6.1 = 0.9 degrees

δ_3 = 13.2 - 13.0 = 0.2 degrees

4. $\sigma(0)$ = .317

$\sigma(90)$ = .104

$\sigma(180)$ = .058

5. σ_{tot} = 1.62

REFERENCES

1. Goldberg, A., Schey, H. M., and Schwartz, J. L., "Computer-Generated Motion Pictures of One Dimensional Quantum—Mechanical Transmission of Reflection Phenomena," *Am. Journal of Physics, 35,* 177, March 1967.

2. Peckham, H. D., *Computers, BASIC, and Physics,* Addison-Wesley, Reading, Mass., 1971.

3. Carnahan, B., Luther, H. A., and Wilkes, J. O., *Applied Numerical Methods,* John Wiley and Sons, New York, N.Y., 1969.